SHOBHIT NIRWAN'S

HYDROCARBONS

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STUDENTS

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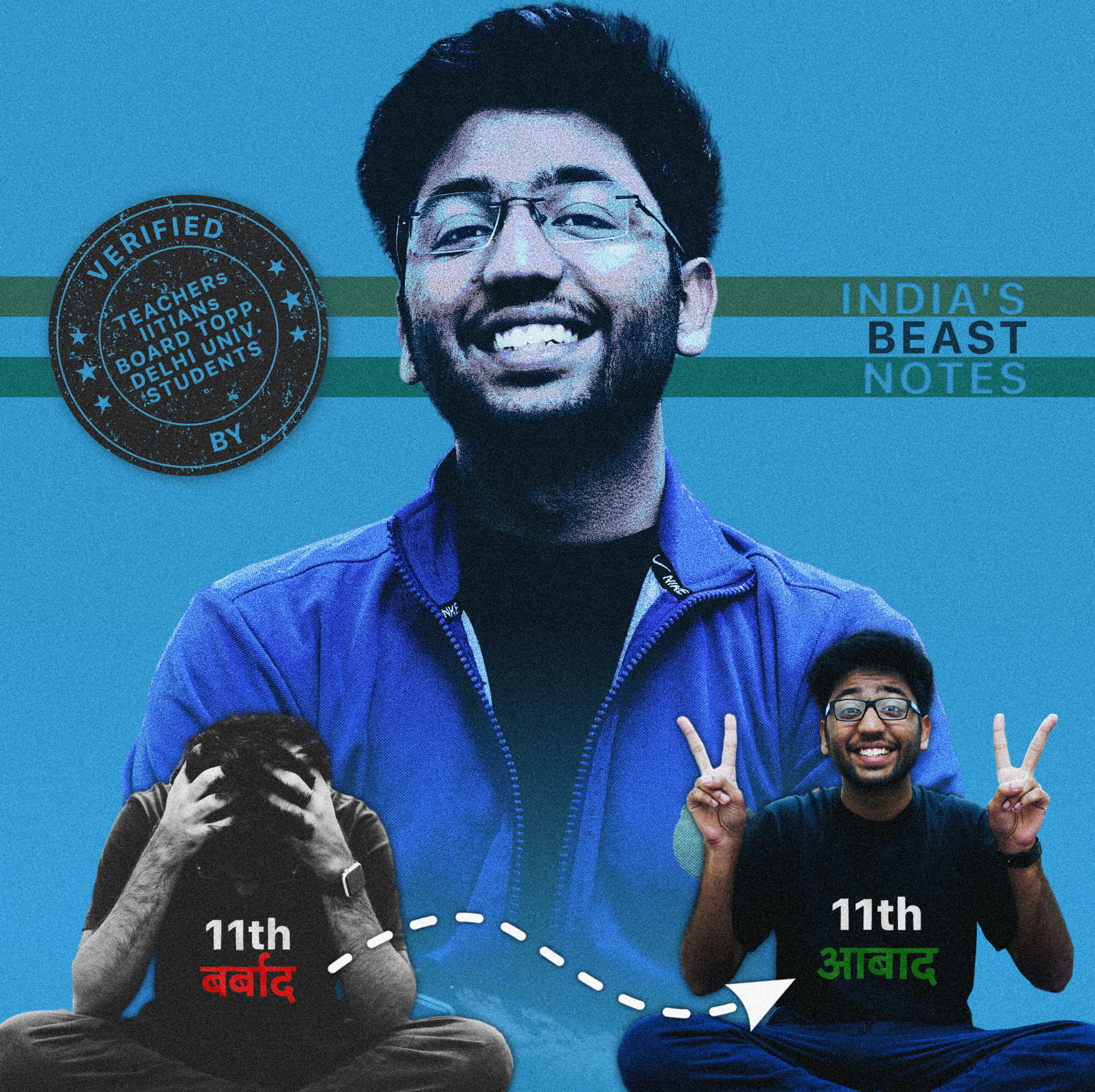
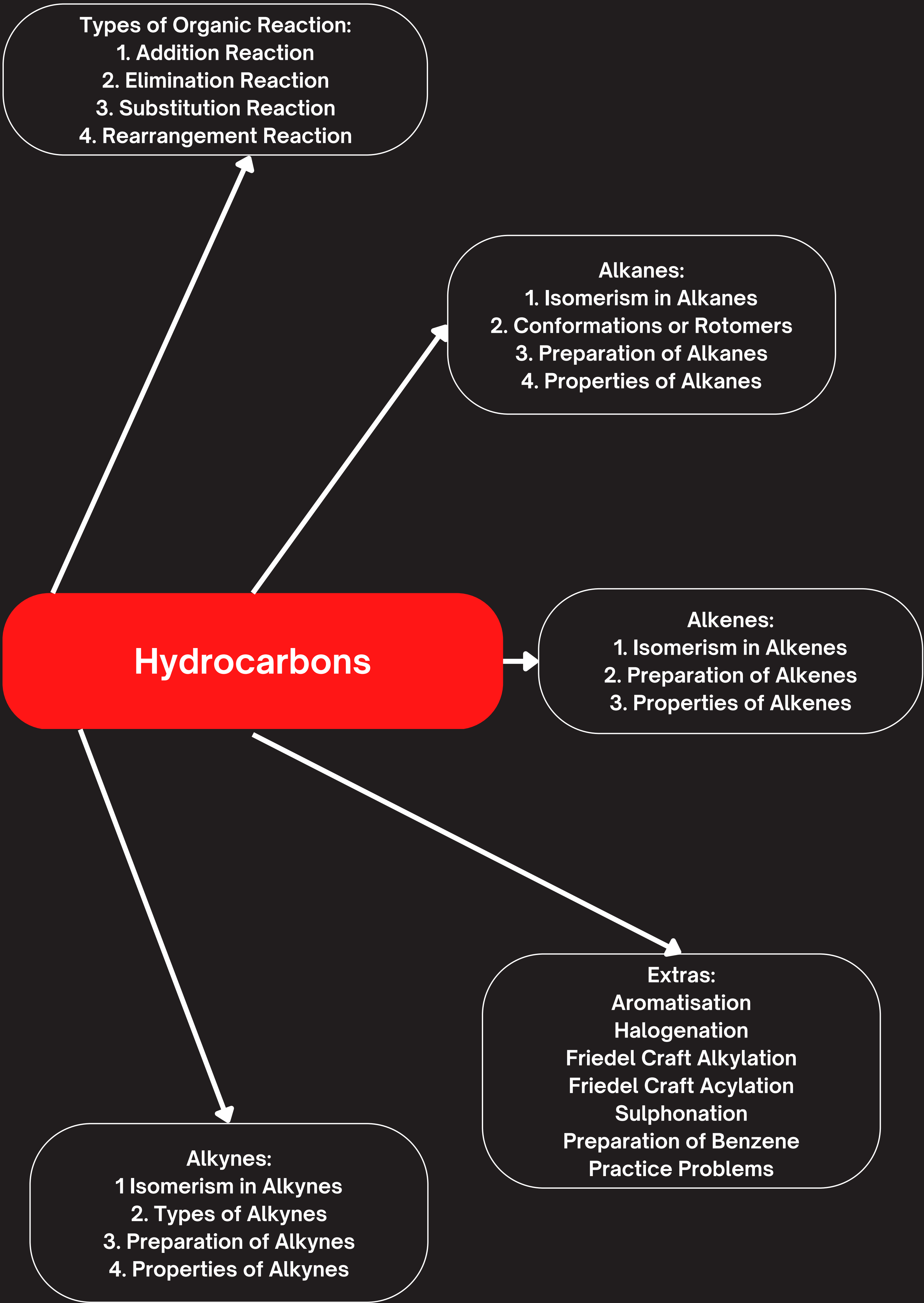
NOTES




Hydrocarbons
Types of Organic Reaction:
1. Addition Reaction
2. Elimination Reaction
3. Substitution Reaction
4. Rearrangement Reaction
Alkanes:
1. Isomerism in Alkanes
2. Conformations or Rotomers
3. Preparation of Alkanes
4. Properties of Alkanes
Alkenes:
1. Isomerism in Alkenes
2. Preparation of Alkenes
3. Properties of Alkenes
Extras:
Aromatisation
Halogenation
Friedel Craft Alkylation
Friedel Craft Acylation
Sulphonation
Preparation of Benzene
Practice Problems
Alkynes:
1 Isomerism in Alkynes
2. Types of Alkynes
3. Preparation of Alkynes
4. Properties of Alkynes

Hydrocarbons

Types of Organic Reactions:

1.) Addition Reaction- A reaction in which two or more reactants combine together to give a single product is called an addition reaction.

Example: CH2=CH2 + H2 ----------> CH3-CH3

- **There are 3 types of addition reactions:**

a.) Electrophilic addition reaction- only alkenes and alkynes give this type of reaction.

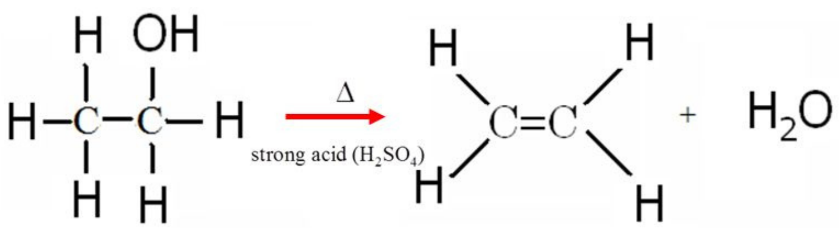
Example: CH3=CH3 + HCl -------------> CH3-CH2Cl

b.)Free-radical substitution reaction- When alkene and alkyne react with HBr in the presence of peroxide.

Example: CH2=CH2 + HBr -------------> CH3-CHBr

c.)Nucleophilic addition reaction- In case of polar multiple bonds.

2.) Elimination Reaction- A reaction in which small molecules like water, HX etc are removed from the reaction is called an elimination reaction.



3.) Substitution Reaction- A type of reaction in which an atom or group of atoms is replaced by another atom or group of atoms is called a substitution reaction.

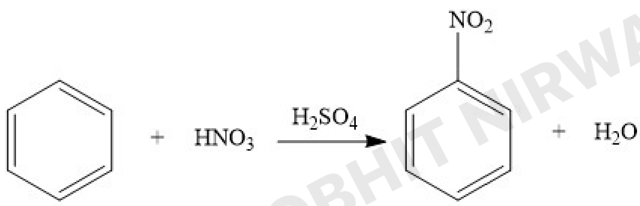
- **There are 3 types of substitution reactions:**

a) Substitution nucleophilic reaction (SN reaction): In this reaction, a strong nucleophile replaces the weak nucleophile from the reactant molecule.

Example: CH3−Cl+KOH→CH3−OH+KCl

b) Electrophilic substitution reaction: Substitution reactions that are brought about by electrophiles are called SE reactions. (only on benzene rings)

Example:



c) Free-radical substitution reaction: When alkanes react with dihalogen in the presence of heat or light.

Example: CH3 + Cl2 ----------------> CH2Cl + HCl (UV over arrow)

4.) Rearrangement Reaction- Reactions involving the migration of an atom or group from one atom to another within the same molecule are called rearrangement reactions.

CH3
|
CH3 - C - CH3 - OH --------------> CH3 - C = CH - CH3
|
CH3

(arrow labelled: Conc. H2SO4, △)

CH3 (on the C of the product)

+ H2O

Q. Classify the following reactions in one of the reaction type studied in this unit

(a) $CH_3CH_2Br + HS^- \rightarrow CH_3CH_2SH + Br^-$

(b) $(CH_3)_2C{=}CH_2 + HCl \rightarrow (CH_3)_2{-}CCl{-}CH_3$

(c) $CH_3CH_2Br + HO^- \rightarrow CH_2{=}CH_2 + H_2O + Br^-$

Solution:

(a) $CH_3CH_2Br + HS^- \rightarrow CH_3CH_2SH + Br^-$

This reaction is called a substitution reaction.

(b) $(CH_3)_2C{=}CH_2 + HCl \rightarrow (CH_3)_2C(Cl)CH_3$

This reaction is called addition reaction.

(c) $CH_3CH_2Br + HO^- \rightarrow CH_2{=}CH_2 + H_2O$

This reaction is called elimination reaction.

Alkanes

- **Saturated Hydrocarbons** (Hydrocarbons containing only single bonds)
- **General formula:** CnH2n+2
- **Simplest hydrocarbon:** Methane, CH_4 (Marshy Gas)

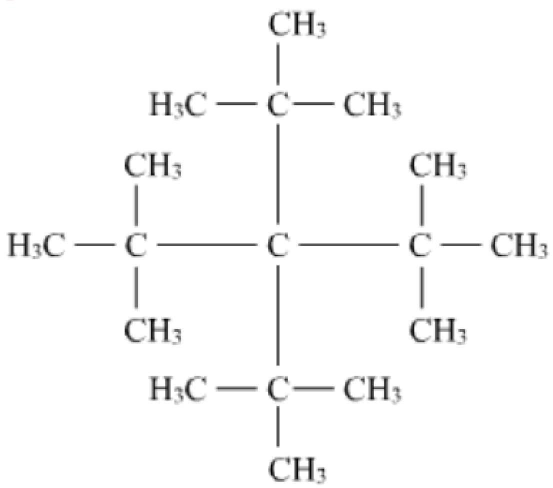
IUPAC naming - (Select Longest chain of carbon atoms)

CH3 - CH2 - CH2 - CH - CH2 - CH - CH3

CH2 - CH2 - CH3 C2H5

3-methyl-5-propyloctance

Tetra-tert-butylmethane



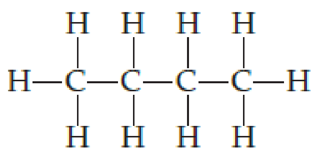
3,3-Ditertiary-Butyl-2,2,4,4-Tetramethylpentane

Isomerism in alkanes

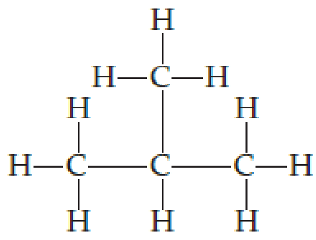
They exhibit two types of isomerism

1.) Chain isomerism: It is a type of structural isomerism

Eg. a) Butane

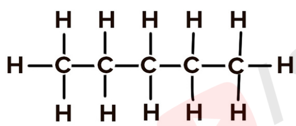


n-butane

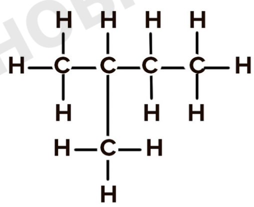


isobutane

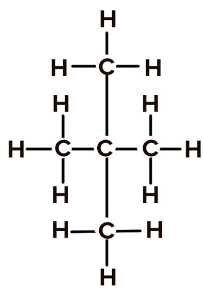
b) Pentane



Pentane

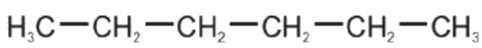


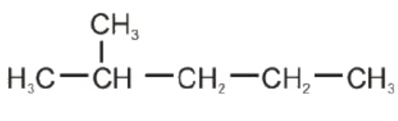
2-Methylbutane

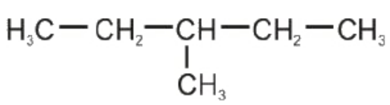


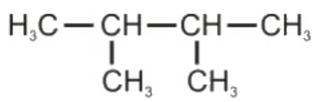
2,2-Dimethyl-propane

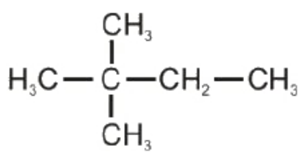
c) Hexane

(1) 

(2) 

(3) 

(4) 

(5) 

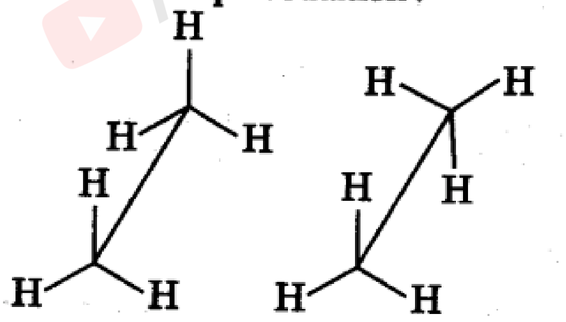
Conformations or Rotomers

- It is a type of stereoisomerism.
- The spatial arrangement of atoms that can be converted into one another by rotation around a C-C single bond is called conformations or conformers or rotamers.

Conformations of ethane: There is an infinite number of conformers of ethane.

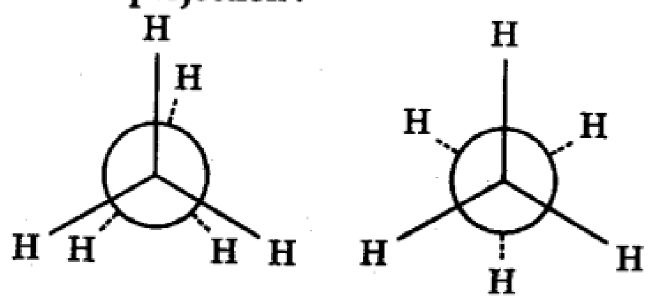
- One conformed in which hydrogen atoms attached to 2 carbon atoms are as close together as possible, is called eclipsed conformation.
- And the other in which hydrogens are as far apart as possible is known as staggered conformation.
- Any other intermediate conformations is called skew conformation.

Sawhorse Representation :



(i) Eclipsed Form(ii) Staggered Form

Newmann projection :



(i) Eclipsed Form (ii) Staggered Form

Stability order of conformers of ethane

Staggered > Skew > Eclipsed

(more stable)

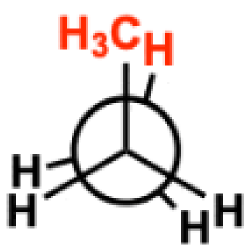
(due to low value of torsional strain)

- **Staggered form has less potential energy**

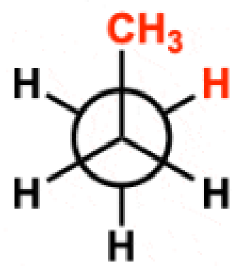
Torsional strain and dihedral angle

- The repulsive interaction between the electron cloud of CH bonds is called torsional strain. The magnitude of torsional strain depends upon the angle of rotation about the C-C bond. This angle is also called the dihedral angle or torsional angle.
- The staggered form has the least torsional strain and eclipsed form has the maximum torsional strain
- The energy between two conformers is of the order of 12.5 KJ/mol which is very small. Therefore, conformers cannot be isolated.

Conformations of propane - Infinite

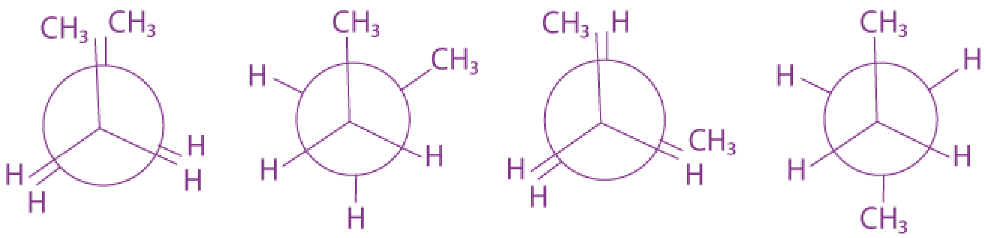


Eclipsed



Staggered

Conformations of butane - Infinite



Fully eclipsed (eclipsed)	gauche (staggered)	eclipsed (eclipsed)	anti (staggered)
$\theta_{Me/Me} = 0^0$	$\theta_{Me/Me} = 60^0$	$\theta_{Me/Me} = 120^0$	$\theta_{Me/Me} = 180^0$

Stability order- Anti > Groche > Eclipsed > Fully eclipsed

Preparation of alkanes

- **From unsaturated hydrocarbons (Hydrogenation)**

$$CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3$$

(addition reaction)

Dihydrogen reacts with alkenes and alkynes in the presence of finally divided catalyst like Ni/Pt/Pd to form alkane. This reaction is known as hydrogenation.

- **From alkyl halides (RX)**

Dihydrogen reacts with alkenes and alkynes in the presence of a finely divided catalyst like Ni/Pt/Pd to form alkane. This reaction is known as hydrogenation.

$$\mathbf{RX + H2 \xrightarrow[\text{dil.HCl}]{\text{Zn}} RH + HX}$$

Eg. CH3CH2Cl + H2 $\xrightarrow[\text{dil.HCl}]{\text{Zn}}$ **CH3CH3 + HCl**

- **Haloalkanes reacts with:**

A) Alkyl halides (expect alkylflouride): On reduction with zinc and dil.HCl to give alkane

eg. $CH3Br + H2 \xrightarrow[H+]{Zn} CH4 + HBr$

B) Wurtz Reaction: Alkyl halides react with sodium metal in the presence of dry ether to give a symmetrical alkene containing an even number of carbon atoms. This reaction is known as Wurtz reaction.

eg.

$$2RX + 2Na \xrightarrow{\text{Dry ether}} R\text{-}R + 2NaX$$

eg. $$2CH_3Cl + 2Na \xrightarrow{\text{Dry ether}} CH_3 + CH_3 + 2NaCl$$

$$2CH_3CH_2Br + 2Na \xrightarrow{\text{dry ether}} CH_3CH_2\text{-}CH_2CH_3 + 2NaBr$$

$$2CH_3\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}CH_2\text{-}Cl + 2Na \xrightarrow{\text{dry ether}} CH_3\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}CH_2\text{-}CH_2\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}CH_3 + 2NaCl$$

Limitations of Wurtz Reaction

This method is used to obtain an alkene containing an even number of carbon atoms.

Role of dry ether:

Haloalkanes are highly soluble in ether and sodium metal does not react with ether due to the absence of acidic hydrogen in ether.

Q) What will happen if two different halides are taken in the Wurtz reaction?
Solution: A mixture of three products are obtained.

From carboxylic acids:

- **RCOOH + NaOH -------------------> RCOONa + H2O**

Sodium Carboxylate

- **RCOOH + KOH -------------------> RCOOK + H2O**

potassium
Carboxylate

Decarboxylation:

$$\underset{\text{Sodium ethanoate}}{CH_3COONa} + \underset{\text{Sodium hydroxide}}{NaOH} \xrightarrow[\text{Heat}]{CaO} \underset{\text{Methane}}{CH_4} + \underset{\text{Sodium carbonate}}{Na_2CO_3}$$

Sodium salts of carboxylic acid on heating with soda lime (mixture of NaOH & CaO in the ratio of 3:1) gives alkanes containing one carbon atom less than the carboxylic acid. This process of elimination of CO2 from a carboxylic acid is known as decarboxylation.

Q.) Sodium salt of which acid will be needed for the preparation of propane by decarboxylation.

Sodium salt of butanoic acid will be needed for the preparation of propane.

Q) What happens: HCOOH(aq)+NaOH(aq)
Solution: H2 + Na2CO3

Kolbe's electrolytic method

An aqeuous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms at the anode.

$$\underset{\text{Sodium acetate}}{2CH_3COO^-Na^+} + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH \qquad (13.9)$$

Mechanism

i) $2CH_3COO^-Na^+ \rightleftharpoons 2CH_3-\overset{\overset{O}{\|}}{C}-O^- + 2Na^+$

ii) **At anode:**

$$\underset{\text{Acetate ion}}{2CH_3-\overset{\overset{O}{\|}}{C}-O^-} \xrightarrow{-2e^-} \underset{\text{Acetate free radical}}{2CH_3-\overset{\overset{O}{\|}}{C}-\dot{\ddot{O}}:} \longrightarrow \underset{\text{Methyl free radical}}{2\dot{C}H_3} + 2CO_2\uparrow$$

iii) $H_3\dot{C} + \dot{C}H_3 \longrightarrow H_3C-CH_3\uparrow$

iv) **At cathode :**

$H_2O + e^- \rightarrow {}^-OH + \dot{H}$

$2\dot{H} \rightarrow H_2\uparrow$

Q.) Methane cannot be prepared this way, why?

This method is used to prepare that alkane containing even number of carbon atoms wherear methane contains odd number of carbon atoms.

Extra reactions of preparations of alkanes

a) Sabatier and Senderm's reactions:

The hydrogenation of unsaturated hydrocarbons using a nickel catalyst at 523-573K is known as Sabatier and Senderm's reaction.

$$CH_2 = CH_2 + H_2 \longrightarrow CH_3 - CH_3$$

b) Grignard's Reagent Reaction

Haloalkanes react with magnesium metal in the presence of dry ether to form alkyl magnesium halide. This is called Grignard's reagent reaction.

RX + Mg -------------> RMgX

Haloalkane — Alkyl Magnesium Halide

Grignard reagents react with water or alcohol or terminal alkynes to give alkanes

RMgX + H2O -----------------> RH + Mg(OH)x

Alkane

RMgX + R'OH --------------------> RH + Mg(OR')X

Alcohol — Alkane

Physical Properties of Alkanes

a.) Solubility- According to "like dissolves like" concept alkanes are non-polar are dissolved in non-polar solvents like ether, benzene, CCl_4, etc but they are insoluble in water. Solubility in non-polar solvent increase with increase in size of the alkyl group.

b) Boiling Point- Alkenes have low boiling point due to presence of weak Van der Waals force amongst its molecules.

- Boiling point of alkanes increases with increase in molecular mass of alkanes.

$$CH_4 < CH_3CH_3 , CH_3CH_2CH_3 < CH_3CH_2CH_2CH_3$$

- Among isomeric alkanes, straight-chain compounds have a larger surface area and branched-chain compounds have less surface area. The magnitude of Van der Waals forces increases with the increase in its surface area. Therefore boiling points of straight-chain compounds are higher than those of branched-chain compounds.

$$CH_3CH_2CH_2CH_3 > \underset{\underset{\displaystyle CH_3}{|}}{CH_3} - CH - CH_2CH_3 > CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_3$$

d) Melting point (similar to boiling point)

- **Exceptions in melting point: n-Alkanes containing even no of carbon atoms are symmetrical and very closely packed in their lattice. Therefore n-alkanes containing even number of carbon atomshave higher melting points than n-alkanes containing odd no. of carbon atoms (adjacent alkane)**

e) Physical state- Amongst the straight-chain alkanes, the first four members are gases, the next thirteen are liquids and higher members are solids.

f) Density- Density of alkane is less than that of water.

Chemical Properties of Alkanes

Alkanes are less reactive due to presence of strong C-C bonds and C-H bond. Therefore alkanes are also called paraffins (latin word means para-little affinis-affinity or reactivity) Some important reactions of alkanes are:

a.) **Combustion:**

$$CH_4(g)+2O_2(g) \rightarrow CO_2(g)+2H_2O(l); \quad \Delta_c H^{\ominus} = -890 \text{ kJ mol}^{-1} \quad (13.17)$$

$$C_4H_{10}(g)+13/2\ O_2(g) \rightarrow 4CO_2(g)+5H_2O(l); \quad \Delta_c H^{\ominus} = -2875.84 \text{ kJ mol}^{-1} \quad (13.18)$$

The general combustion equation for any alkane is :

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \rightarrow nCO_2 + (n+1)H_2O$$

- Due to the evolution of large amount of heat during combustion, alkanes are used as fuels.
- During incomplete combustion (Lack of air) of alkanes with insufficient amount of air or dioxygen, carbon black is formed which is used in the manufacture of in, printer ink.

$$CH_4(g)+O_2(g) \xrightarrow[\text{combustion}]{\text{Incomplete}} C(s)+2H_2O(l)$$

b) Controlled Oxidation: It takes place in the presence of a catalyst.

$$2CH_4 + O_2 \xrightarrow[523\text{ K}/100\text{ atm}]{Cu} \underset{\text{(Methanol)}}{2CH_3OH}$$

$$CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} \underset{\text{(Methanal)}}{HCHO} + H_2O$$

$$2CH_3CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} \underset{\text{(Ethanoic Acid)}}{2CH_3COOH} + 2H_2O$$

- Alkanes having tertiary hydrogen atom can be oxidised to corresponding alcohols by potassium permangnate (KmNO4)

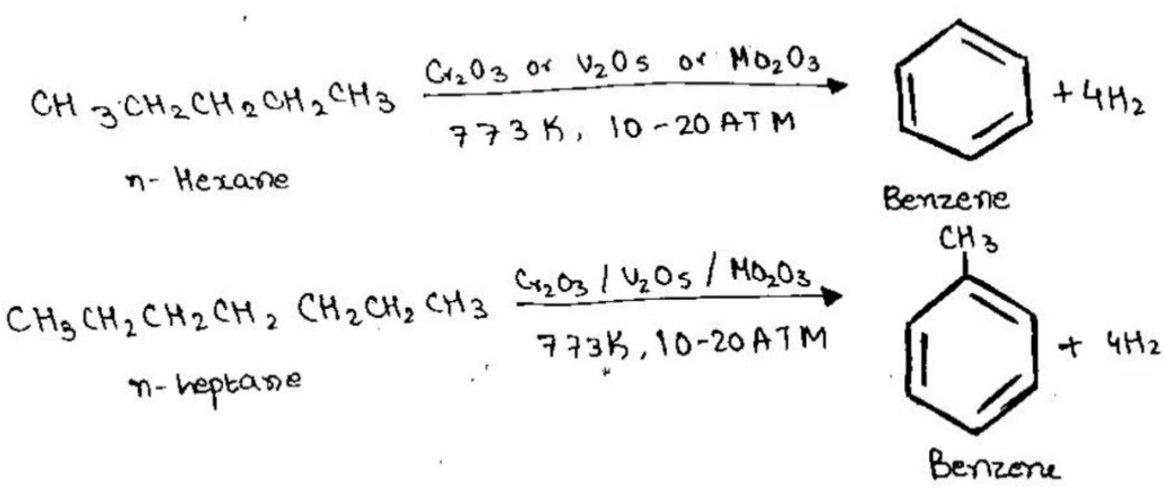
$$\underset{\text{2-Methylpropane}}{(CH_3)_3CH} \xrightarrow[\text{Oxidation}]{KMnO_4} \underset{\text{2-Methylpropan-2-ol}}{(CH_3)_3COH}$$

c) Isomerisation: n-Alkanes on heating in the presence of anhydrous aluminum chloride and hydrogen chloride gas isomerize to branched-chain alkanes. This reaction is known as isomerization reaction.

$$\underset{n\text{-Hexane}}{CH_3(CH_2)_4CH_3} \xrightarrow{\text{Anhy. } AlCl_3/HCl}$$

$$\underset{\text{2-Methylpentane}}{CH_3\underset{\substack{| \\ CH_3}}{CH}-(CH_2)_2-CH_3} + \underset{\text{3-Methylpentane}}{CH_3CH_2-\underset{\substack{| \\ CH_3}}{CH}-CH_2-CH_3}$$

d) Aromatisation: n-Alkanes having six or more carbon atoms on heating to 773K at 10-20 atmospheric pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina get dehydrogenated and cyclised to benzene and its homologues. This reaction is known as aromatization or reforming.



e) Reaction with steam: Alkanes react with steam to form syn gas or water gas.

$$CH_4 + H_2O \xrightarrow[\Delta]{Ni} CO + 3H_2$$

f) Pyrolysis or cracking: Higher alkanes on heating to higher temperature decompose into lower alkanes, alkenes, etc. Such a decomposition reaction into smaller fragments by the application of heat is called pyrolysis or cracking.

$$C_6H_{14} \xrightarrow{773K} \begin{cases} \underset{\text{Propene}}{C_3H_6} + \underset{\text{Ethene}}{C_2H_4} + CH_4 \\ C_4H_8 + C_2H_6 \\ C_6H_{12} + H_2 \end{cases}$$

- **Pyrolysis occurs by the free-radical reaction.**
- **Preparation of oil gas or petrol gas from kerosene oil or petrol involves the principle of pyrolysis.**

$$\underset{\text{Dodecane}}{C_{12}H_{26}} \xrightarrow[973\ k]{Pt/Pd/Ni} \underset{\text{Heptane}}{C_7H_{16}} + \underset{\text{Pentene}}{C_5H_{10}} + \text{other products}$$

g) Substitution reaction (Free radical substitution): A reaction in which a hydrogen atom of an alkane is replaced by an atom or group of atoms is called substitution.

- **eg. Halogenation, Nitration, Sulphonation**
- **Halogenation of alkanes:** Halogenation of alkanes is carried out by treating it with a dihalogen (X2) in the presence of ultra-violet light or heating at 523-573K.

eg $RH + X_2 \xrightarrow[\text{uv light}]{} RX + HX$

Monohalogenation

i) $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$

ii) $CH_4 + Br_2 \longrightarrow CH_3Br + HBr$

iii) $CH_4 + I_2 \longrightarrow CH_3I + HI$

Iodination is very slow and reversible reaction. It can be carried out in the presence of oxidising agents like HIO3 (iodic acid) or HNO3 (Nitric acid) which oxidise HI into I2 and shifts the equilibrium in the forward direction.

$$HIO_2 + 5HI \longrightarrow 3I_2 + 3H_2O$$

$$2HNO_3 + 2HI \longrightarrow I_2 + 2NO_2 + 2H_2O$$

$$CH_3 + F_2 \longrightarrow CH_3F + HF$$

The fluorination of alkanes is too vigorous to be controlled under ordinary conditions. Fluorination of alkanes can be carried out by diluting F2 with an inert gas such as N2 or Argon.
Alternatively, Fluoroalkanes are obtained by Swarts Reaction:

Swarts Reaction-

$$CH_3Cl + AgF \xrightarrow{\Delta} CH_3F + AgCl$$

$$2CH_3Br + Mg_2F_2 \xrightarrow{\Delta} 2CH_3F + Mg_2Br_2$$

- **Dihalogenation:**

$$CH_4 + 2Cl_2 \longrightarrow CH_2Cl_2 + 2HCl$$

$$CH_4 + 2Br_2 \longrightarrow CH_2Br_2 + 2HBr$$

Trihalogenation:

$$CH_4 + 3Cl_2 \longrightarrow \underset{\substack{\text{chloroform} \\ \text{(1,1,1 trichloromethane)}}}{CHCl_3} + 3HCl$$

$$CH_4 + 3Br_2 \longrightarrow \underset{\text{Bromoform}}{CHBr_3} + 3HBr$$

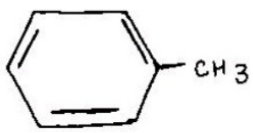
Tetrahalogenation:

$$CH_4 + 4Cl_2 \longrightarrow \underset{\text{Tetrachloromethane}}{CCl_4} + 4HCl$$

$$CH_4 + 4Br_2 \longrightarrow \underset{\text{Tetrabromomethane}}{CBr_4} + 4HBr$$

For major product of Halogenation: Replace hydrogen atom by halogen atom in the following position:

Benzylic hydrogen



$>$ Allylic hyd. $CH_2 = CH - CH_3$ $>$ 3° hydrogen $CH_3 - \underset{\substack{| \\ CH_3}}{CH} - CH_3$ $>$ 2° hydrogen $CH_3CH_2CH_3$

$>$ 1° hydrogen CH_3CH_3

eg. Write the major products of the following reactions

i) $$CH_3CH_2CH_3 + Cl \longrightarrow \underset{\text{(Major)}}{CH_3 - \overset{\overset{Cl}{|}}{CH} - CH} + HCl$$

ii) $$CH_2 = CH - CH_2 - CH_2 - CH_3 + Cl_2 \longrightarrow \underset{\text{(Major)}}{CH_2 = CH - \overset{\overset{Cl}{|}}{CH} - CH_2 - CH_3} + HCl$$

8) For all products of halogenation:

Replace all types of hydrogen atoms with halogen atoms.

Never replace the hydrogen atom with double bonded or triple-bonded carbon atom

Q.) Write all the products of monochlorination of the following:

① $CH_3CH_2CH_3$

$$CH_3CH_2CH_3 + Cl_2 \xrightarrow{h\nu} \underbrace{CH_3CH_2CH_2Cl + CH_3CH(Cl)CH_3}_{} + HCl$$

(2 products)

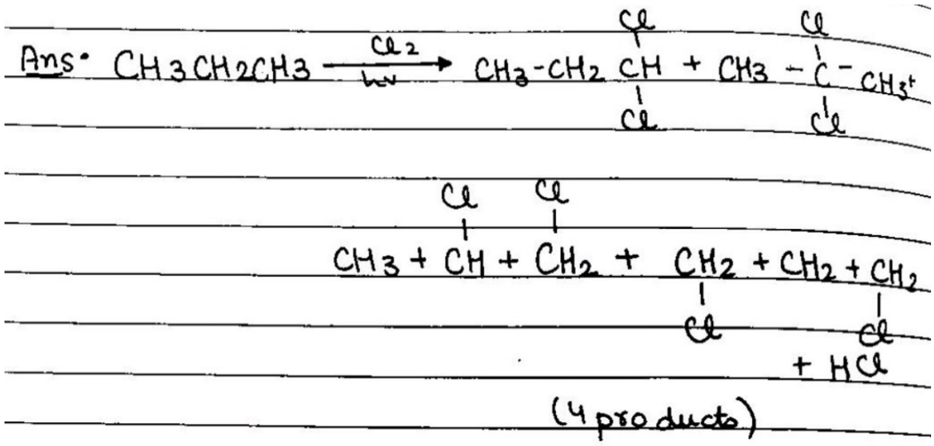
② $CH_3-CH(CH_3)-CH_2-CH_3$

$$CH_3-CH(CH_3)-CH_2-CH_3 \xrightarrow[h\nu]{Cl_2} CH_3-CH(CH_3)-CH_2-CH_2Cl + CH_3-CH(CH_3)-CH(Cl)-CH_3 +$$

$$CH_3-C(Cl)(CH_2)-CH_2-CH_2 + CH_2(Cl)-CH(CH_3)-CH_2CH_3 + HCl$$

(4 products)

Q.) Write the structure of dihalogenation derivatives of propane



It involves 3-steps

1.) Initiation Step- Generation of free-radical

$$Cl-Cl \xrightarrow[\text{homolysis}]{h\nu} \dot{Cl} + \dot{Cl}$$

(chlorine free radical)

2.) Propagation: Chlorine free radicals attack methane molecules to generate methyl free radicals with the formation of HCl. Methyl free radical attacks the chlorine molecule to form another chlorine free radical with the formation of CH3Cl

$$H_3C-H + \dot{Cl} \xrightarrow{h\nu} \dot{C}H_3 + HCl$$

(Methyl Free Radical)

3.) Termination: The reaction stops after sometimes due to the following side reactions.

$$\dot{Cl} + \dot{Cl} \longrightarrow Cl_2$$

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3$$

$$\dot{C}H_3 + \dot{Cl} \longrightarrow CH_3Cl$$

The reaction above helps us to understand the reaction for the formation of ethane as a by-product during chlorination of methane

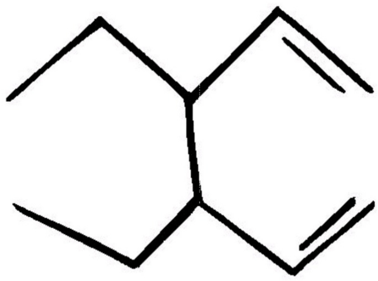
Alkenes

- Unsaturated hydrocarbons with double bonds.
- General Formula- C_nH_{2n}
- Simplest alkene- $CH_2=CH_2$ (Ethene), CN (Ethylene)

IUPAC Nomenclature:

- **$CH_3-CH=CH_2$ (Prop-1-ene)**
- **$CH_3-CH=CH-CH_3$ (But-2-ene)**
- **$CH_2=CH-CH=CH_2$ (Buta-1,3-diene)**
- **Penta-1,3-diene**

- **3,4-diethyl hexa-1,5 diene**



$CH_2 = C(CH_2CH_2CH_3)_2$

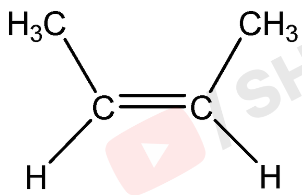
2-Propylpentene

$$
\begin{array}{l}
CH_2 = \underset{\displaystyle\overset{|}{CH_2}}{C} - CH_2 - CH_2 - CH_3 \\
\qquad\;\;\; | \\
\qquad\;\; CH_2 \\
\qquad\;\;\; | \\
\qquad\;\; CH_3
\end{array}
$$

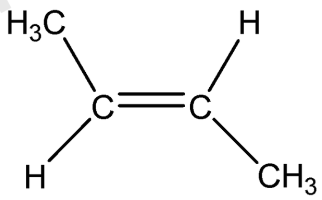
Isomerism in alkenes

1.) Chain Isomerism
2.) Positional isomerism
3.) Functional group isomerism

4.) Geometrical isomerism: It is a type of stereoisomer. These isomers that have the same structural formula but differ in the relative spatial arrangement of atoms or groups around double bonds are called geometrical isomers and this phenomenon is known as geometrical isomerism.
The isomers in which similar atoms or group of atoms are on the same side of the double bond is called cis-isomer whereas isomers in which similar atoms or groups lie on the opposite side of the double bond is called trans-isomers.
This isomerism is called cis-trans isomerism.



cis-but-2-ene



trans-but-2-ene

Conditions for geometrical isomerism:-
If different groups are bonded with carbon atoms of double bond or ring.

Q.) Which of the following compounds show geometric isomerism?

a.) CH2=CHBr - Not show

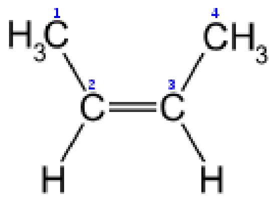
b.) CH3CH=C(CH3)2 - Not show

c.) CH3CH=CHC2H5 - Show

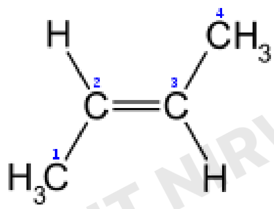
d.) CH3CH=CHCH3 - Show

Q.) Draw cis-trans isomers of the following compounds

a.) CH3CH=CHCH3

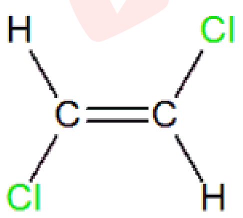


cis-but-2-ene

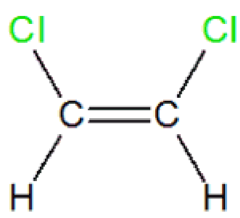


trans-but-2-ene

b.) CHCL= CHCl

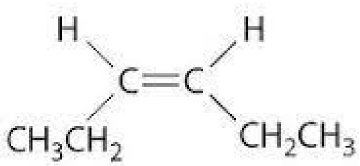


trans-1,2-dichloroethene

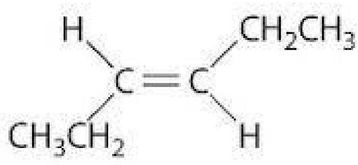


cis-1,2-dichloroethene

c.) Hex-3-ene



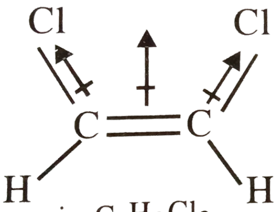
Cis



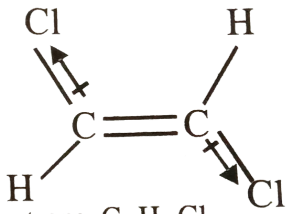
Trans

Properties of cis & trans isomers

1.) Dipole moment: In general cis-isomers of an alkene is found to be more polar than the trans isomers.



cis–$C_2H_2Cl_2$
($\mu \neq 0$)



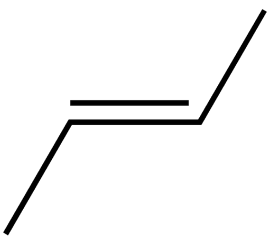
trans–$C_2H_2Cl_2$
($\mu = 0$)

The dipole moment of cis-isomer is more than of trans-isomers

2.) Solubility: According to "like dissolve like", cis isomer is more soluble in water (polar solvent) than trans-isomer. This is because cis-isomer is polar.

3.) Boiling Point: Boiling point of cis-isomers is higher than that of trans-isomers. This is because cis-isomer is polar and trans-isomer is non-polar. Dipole-dipole interaction is present in cis-isomers whereas dispersion force is present in trans-isomers. Dipole-dipole interaction is a stronger intermolecular force than dispersion forces.

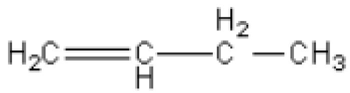
4.) Melting Point and stability: Trans-isomers are more symmetrical and closely packed in their crystal lattice. Therefore, trans-isomers have higher melting point and greater stability than cis-isomers.



Trans-isomers

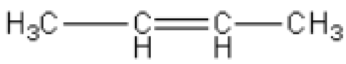
Cis-isomers

Q.) Draw the structures of all isomers of alkene of molecular formula C4H8

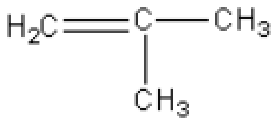
(A) 

1-butene

Total number of isomers: 4

(B) 

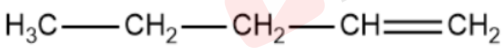
2-butene

(C) 

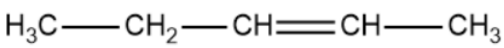
2-methylprop-1-ene

Q.) Draw the structures of all structural isomers of alkene with molecular formula C5H10

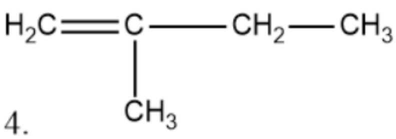
1.



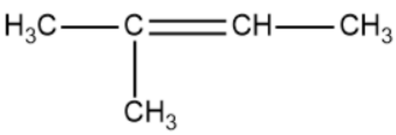
2.



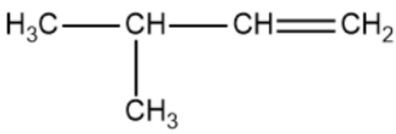
3.



4.

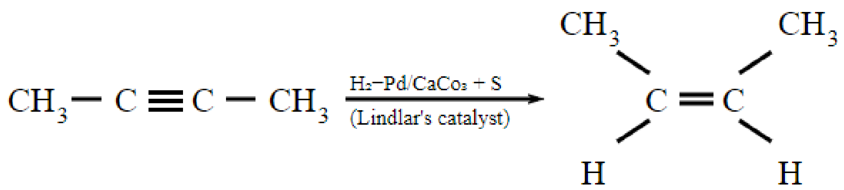


5.



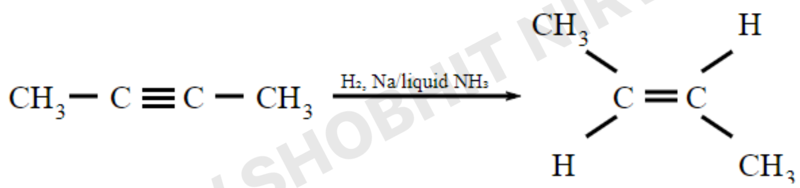
Preparation of alkenes

1.) By partial reduction of alkynes: Alkenes on partial reduction with the calculated amount of dihydrogen in the presence of palletized charcoal partially deactivated with poisons like sulfur, compounds, or quinoline give alkenes (cis-alkene)



Note: Partially deactivated palladised charcoal is known as Lindlar's catalyst.

Birch reduction: Alkynes on reduction with sodium in liquid ammonia form trans-alkanes. This process is called Birch Reduction.



2.) From Alkyl Halides:

- **β-elimination reaction:** Alkyl halides on heating with alcoholic KOH or alcoholic NaOH eliminate one molecule of halogen acid (HX) to form an alkene. This reaction is known as dehydrohalogenation. This is an example of β-elimination reaction.

$$CH_3-CH_2-Br + NaOH \xrightarrow{\Delta} CH_2=CH_2 + NaBr + H_2O$$

$$CH_3-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_3 + KOH \xrightarrow{\Delta} CH_3-CH=CH-CH_3 + KCl + H_2O$$

3.) Saytzeff's rule: In dehydrohalogenation reaction, alkenes is a major product that is highly substituted.

$$CH_3-CH_2-\underset{\displaystyle |}{\overset{Br}{C}}H-CH_3 + KOH \xrightarrow{\Delta}$$

$$\underset{\text{(Minor)}}{CH_3-CH_2-CH=CH_2} + \underset{\text{(Major)}}{CH_3-CH=CH-CH_3} + KBr + H_2O$$

3.) From alcohol:

Alcohols on heating with concentrated H2SO4 forms alkenes with the elimination of one molecule of H2O. This reaction is known as the acidic dehydration of alcohols.

$$CH_3CH_2OH \xrightarrow[\Delta]{\text{conc. } H_2SO_4} CH_2=CH_2 + H_2O$$

4.) From Vicinal dihalides: Vicinal dihalides on treatment with zinc metal loss a molecule ZnX2 to form an alkene. This reaction is known as dehalogenation,

$$CH_2Br-CH_2Br + Zn \longrightarrow CH_2=CH_2 + ZnBr_2$$

$$CH_3CHBr-CH_2Br + Zn \longrightarrow CH_3CH=CH_2 + ZnBr_2$$

Vicinal dihalide

1,2-dibromopropane

Note: Dihalides in which two halogen atoms are attached to two adjacent carbon atoms are known as vicinal dihalides or Vic-dihalides.

```
CH2 - CH2
 |     |
 Br    Br
```

Dihalides in which two halogen atoms are attached to some carbon atoms are known as geminal dihalides or gem-dihalides.

```
CH3 - CH - CHBr
          |
          Br
```

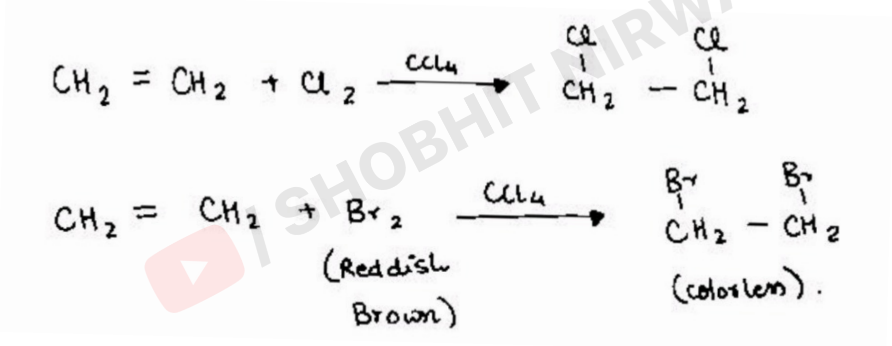
Physical properties of alkenes

Similar to alkanes

Physical State: First three members of alkenes are gases, next 14 are liquid and others are solid.

Chemical Properties: Alkenes are a rich source of loosely held pi-electrons due to which they show electrophilic addition reaction. Therefore, alkenes are more reactive than alkanes. **Some important reactions of alkenes are:**

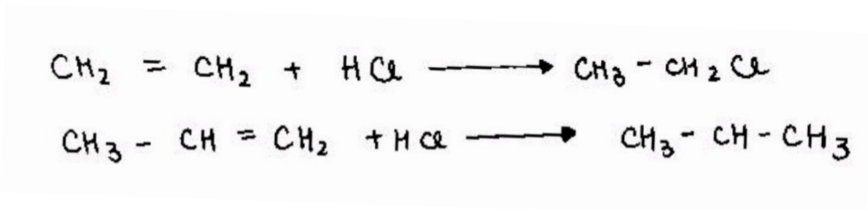
- **Addition of dihydrogen:** Alkenes react with H2 gas in the presence of Ni/Pt/Pd to give alkanes.
- **Addition of Dihalogen:** Alkenes react with dihalogen (Cl2 or Br2) in the presence of CCl4 (or dark) to give VIC-dihalides.



Note:

Test for unsaturation: Alkenes react with Bromine in CCl4 and decolorize its reddish-orange color. This reaction is used in the test for unsaturation.

- **Addition of HX (HCl, HBr, HI):** Alkenes react with HX to give haloalkanes (According to Markovniko's rule)



Note:

1. **In the case of unsymmetrical alkenes with unsymmetrical reagents, apply Markonikov's rule.**
2. **Markonikov's rule- "Negative part of the addendum (adding molecule) gets attached to the carbon which possesses lesser no of hydrogen atoms.**

Mechanism addition of HBr on propene
or
Mechanism of Markonikov's Rules

Hydrogen bromide provides an electrophile, H+ , which attacks the double bond to form carbocation as follows

$$CH_3-CH=CH_2 + H-Br \xrightarrow[-Br]{} CH_3-\overset{+}{C}H-CH_3 + CH_3-CH_2-\overset{+}{C}H_2$$

2° carbocation 1° carbocation

Because 2nd carbocation is more stable than 1st carbocation, therefore, 2nd carbocation is formed at a faster rate. 2nd carbocation reacts with Br- to form the major product.

$$Br^- \quad H_3C-\overset{+}{C}H-CH_3 \longrightarrow H_3C-\underset{\displaystyle Br}{\underset{|}{C}H}-CH_3$$

2-Bromopropane
(major product)

Anti Markonikov's rule or peroxide effect or Kharash effect.

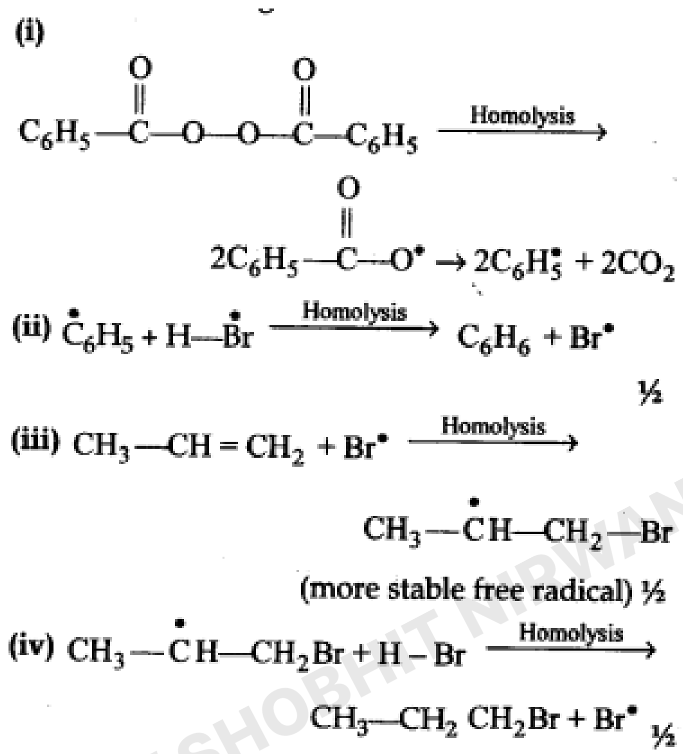
In the presence of peroxide, addition of HBr or assymetrical alkene like propene takes place contrary to the Markonikov's rule

$$CH_3-CH=CH_2+HBr \xrightarrow{(C_6H_5CO)_2O_2} CH_3-\underset{\displaystyle CH_2Br}{\underset{|}{C}H_2}$$

1-Bromopropane

Mechanism of addition of HBr on propene in the presence of peroxides.

Mechanism of the free-radical addition reaction. It takes place as follows:



Note: Peroxide effect is not observed in addition of HF and HCl because H-F and H-Cl bonds are stronger than H-Br bonds and they do not break.

The peroxide effect is not observed in addition to HI because H-I is weaker than the H-Br bond and it provides iodine free radicals which combine to form an I2 molecule instead of adding to the double bond.

(I• + I• -------------> I2)

Addition of sulfuric acid

Alkenes react with cold-concentrated H2SO4 to give alkyl hydrogen sulfate (According to Markonikov's rule)

$$CH_2 = CH_2 + H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-H \longrightarrow CH_3-CH_2-O\,SO_2-OH \text{ or } C_2H_5HSO_4 \qquad (13.44)$$

Ethyl hydrogen sulphate

$$CH_3-CH=CH_2 + HOSO_2OH \longrightarrow CH_3-\underset{\underset{OSO_2OH}{|}}{CH}-CH_3$$

Propyl hydrogen sulphate

Addition of water

Alkenes react with water in the presence of dil.H2SO4 to form alcohol (According to Markonikov's Rule)

eg. $CH_2 = CH_2 + H_2O \xrightarrow{\text{dil. } H_2SO_4} CH_3CH_2OH$

$$CH_3-CH=CH_2 + H_2O \xrightarrow{H^+} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

Propan-2-ol

Oxidation

- Alkenes on reaction with cold, dilute, an aqueous solution of potassium permanganate (Baeyer's reagent) produce vicinal glycols. Decolorization of KMnO4 solution is used as test for unsaturation.

$$\underset{\text{Ethylene}}{H_2C=CH_2} + \underbrace{H_2O + O}_{\text{Baeyer's reagent}} \longrightarrow \underset{\text{Ethylene glycol}}{\underset{\substack{|\\OH}}{CH_2}-\underset{\substack{|\\OH}}{CH_2}}$$

$$\underset{\text{Propylene}}{CH_3-CH=CH_2} + \underbrace{H_2O + O}_{\text{From alkaline } KMnO_4} \longrightarrow \underset{\text{Propylene glycol}}{CH_3-\underset{\substack{|\\OH}}{CH}-\underset{\substack{|\\OH}}{CH_2}}$$

- Acidic KMnO4 or acidic K2Cr2O7 (Potassium dichromate) oxidises alkenes, to ketone and/or acids depending upon the nature of the alkene

Product of alkenes :-

$$CH_2= \longrightarrow CO_2$$

$$RCH= \longrightarrow RCOOH$$

$$R-\underset{\substack{|\\R}}{C}= \longrightarrow R-\underset{\substack{|\\R}}{C}=O$$

eg. $CH_2=CH_2 \xrightarrow[H_2SO_4]{KMnO_4} CO_2$

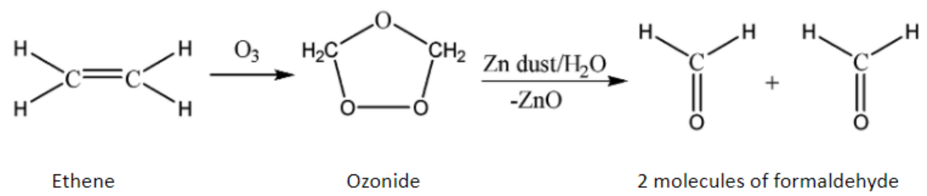
$$CH_3-CH=CH_2 \xrightarrow[H_2SO_4]{KMnO_4} CH_3COOH + CO_2$$

$$CH_3-\underset{\substack{|\\CH_3}}{C}=CH-CH_3 \xrightarrow[H^+]{KMnO_4} CH_3-\underset{\substack{|\\CH_3}}{C}=O + CH_3COOH$$

Ozonolysis

- Alkenes react with ozone to form ozonide which further reductive hydrolysis in the presence of zinc metal to form aldehydes, ketones or both. This reaction is used to detect the position of double bonds in alkenes.

Eg. a)



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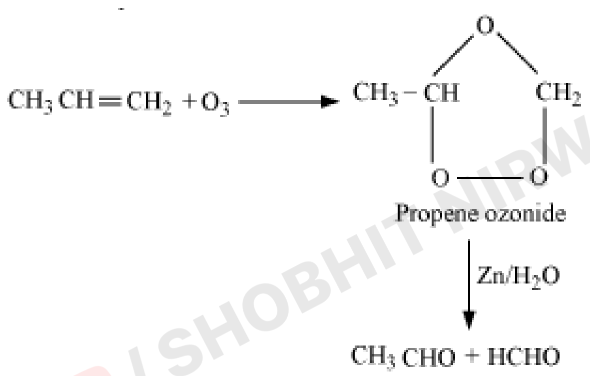

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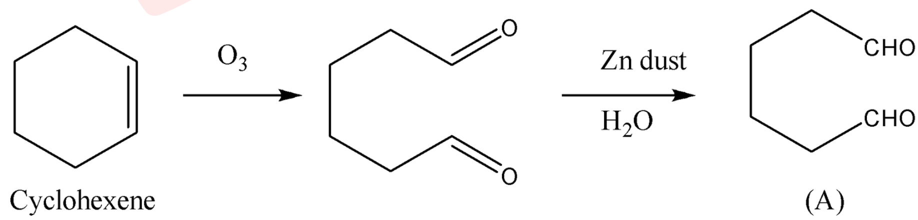


Polymerisation

- Polyethylene is obtained by the combination of a large number of ethene molecules at high temperatures high pressure and in the presence of a catalyst. The large molecule thus obtained are called polymers. This reaction is called polymerization. The simple compounds from which polymers are made are called monomers.

$$n(CH_2{=}CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} -\!\!(CH_2-CH_2)\!\!-_n$$

Polythene

(13.53)

$$n(CH_3-CH{=}CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} -\!\!(\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2)\!\!-_n$$

Polypropene

- Polyalkenes are used for the manufacture of plastic bags, squeeze bottles, toys, pipes, radios and TV cabinets, etc.
- Polypropene is used for the manufacture of milk crates, plastic buckets and other molded articles.

Olefins: Alkenes are also called olefins. **(Greek: olefiant= oil forming)**

Alkynes

- Unsaturated Hydrocarbons containing carbon-carbon triple bonds.
- General formula- CnH2n-2

Common names of alkynes:
H-C≡CH Acetylene
CH3-C≡CH Methylacetylene
CH3CH2-C≡CH Ethylacetylene
CH3 -C≡C-CH3 Dimethylacetylene

Isomerism in alkynes

1. Chain Isomerism
2. Position Isomerism
3. Functional Group Isomerism
4. Ring Chain Isomerism

Types of alkynes:

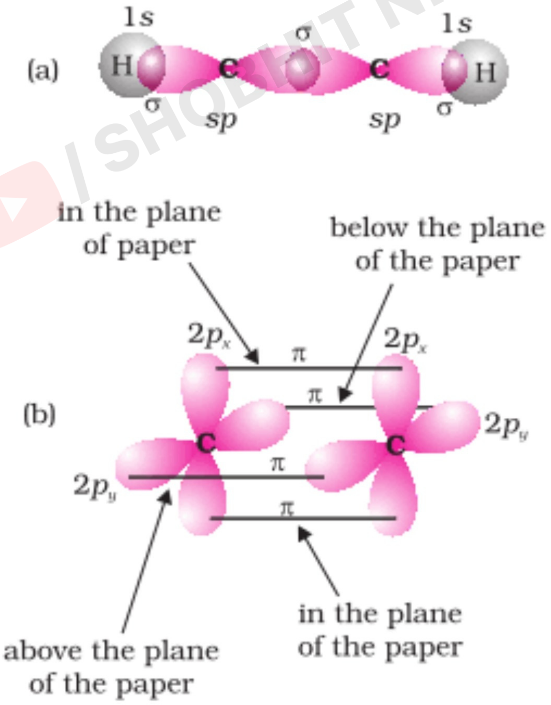
- **Terminal alkynes:** If triple bond is present at the end of the carbon chain. They contain acidic hydrogen

$$CH_3CH_2CH_2{-}C{\equiv}C{-}H$$

- **Non-Terminal alkynes:** If triple bond is present within the carbon chain. They do not contain acidic hydrogen

$$CH_3CH_2CH_2{-}C{\equiv}C{-}CH_2CH_3$$

Structure of triple bond:



$$H \overset{\sigma}{\text{———}} C \overset{\pi}{\underset{\pi}{\overset{\sigma}{\equiv}}} C \overset{\sigma}{\text{——}} H$$

Preparation of alkynes

- **From Calcium carbide (CaC2):**

$$CaC_2 + 2H_2O \longrightarrow \underset{\text{Ethyne}}{C_2H_2} + Ca(OH)_2$$

Preparation of calcium carbide →

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow$$

$$\underset{\text{lime}}{CaO} + \underset{\text{coke}}{3C} \longrightarrow CaC_2 + CO$$

- **From vicinal dihalides:** Vicinal dihalides convert into alkynes as follows:

$$\overset{Br}{\overset{|}{CH_2}} - \overset{Br}{\overset{|}{CH_2}} + KOH \xrightarrow{\Delta} CH_2 = \overset{Br}{\overset{|}{CH}} + KBr + H_2O$$

$$CH_2 = \overset{Br}{\overset{|}{CH}} + \underset{\text{Sodamide}}{NaH_2} \xrightarrow{\Delta} CH \equiv CH + NaBr + NH_3$$

Or

$$\underset{Br}{\underset{|}{CH_2}} - \underset{Br}{\underset{|}{CH_2}} \xrightarrow[\Delta]{KOH} CH \equiv CH + 2KBr + 2H_2O$$

- **Chloroform or Iodoform on heating with silver powder to form ethyne: :**

$$\underset{\textbf{Chloroform}}{2CHI_3} + \underset{\textbf{silver powder}}{6Ag} \xrightarrow{\Delta} \underset{\textbf{Ethyne}}{CH \equiv CH} + 6AgI$$

Physical properties of alkynes

Similar to alkenes

Physical State: First three members are gases and next 8 are liquids.
Homologous- successive members differ by CH2

Chemical Properties: Alkynes are less reactive than alkenes towards electrophilic addition reactions, due to the following reasons:

- **Due to greater electronegativity of sp hybridization** of carbon atoms of a triple bond than sp2 hybridized carbon atoms of a double bond. The pi-electrons of alkynes are more tightly held by the carbon atoms than pi-electrons of alkenes and hence are less easily available for reaction with an electrophile.
- **Due to the cylindrical nature of the pi-electrons cloud of alkynes,** the pi-electrons of a triple bond are more delocalized than the pi-electrons of a double bond.

Reactivity order of alkane, alkene, and alkynes:
Alkane < Alkyne < Alkene

Important reactions of alkynes:

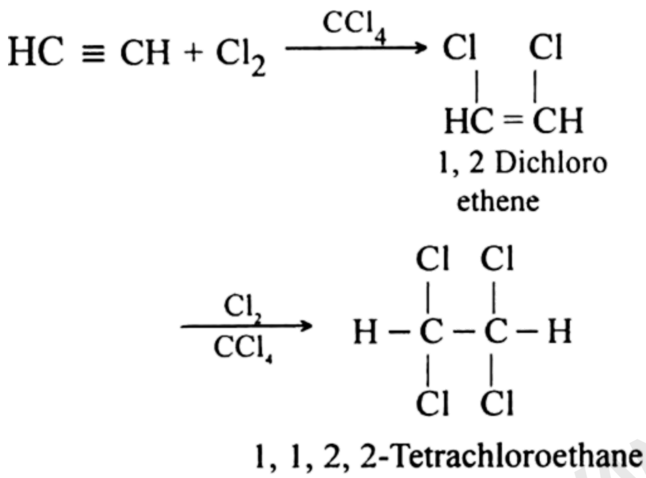
Electrophilic addition reaction

- **Addition of dihydrogen**

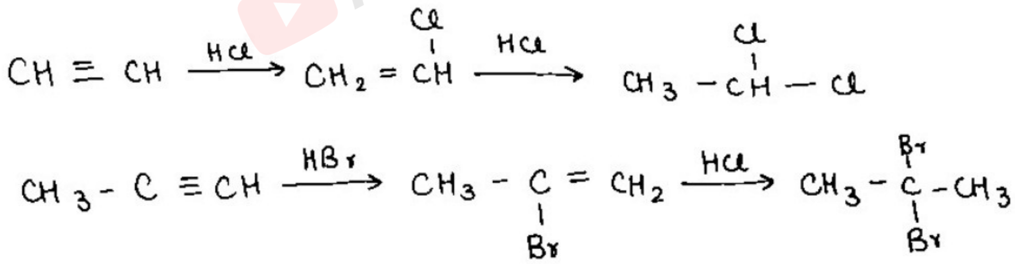
$$\underset{\text{Ethyne}}{CH\equiv CH} + H_2 \xrightarrow{Pd/C} \underset{\text{Ethene}}{CH_2=CH_2} \quad (13.32)$$

$$\underset{\text{Propyne}}{CH_3-C\equiv CH} + H_2 \xrightarrow{Pd/C} \underset{\text{Propene}}{CH_3-CH=CH_2}$$

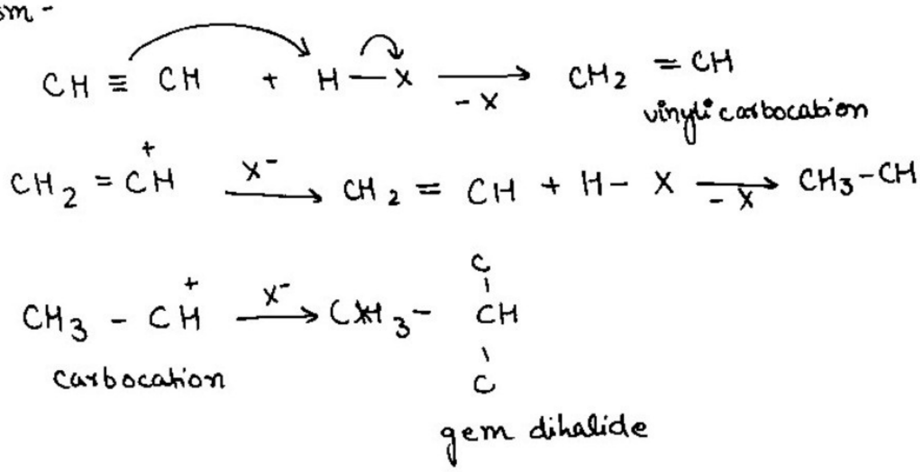
- **Addition of dihalogen in the presence of CCl4:** This reaction is used for test of unsaturation



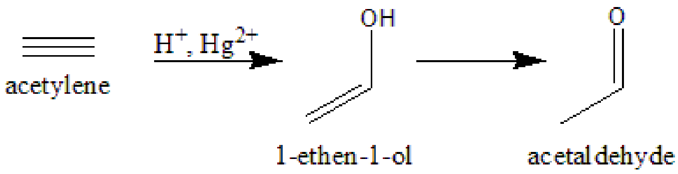
- **Addition of HX (HCl,HBr, HI) :** Alkynes react with HX to give geminal dihalide (According to Markonikov's rule)

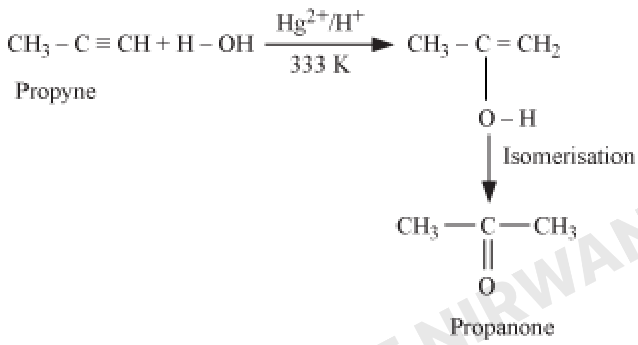


Mechanism -



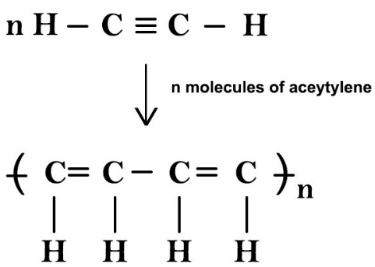
- **Addition of water:** Alkynes are insoluble in water but they react with water in the presence of MgSO4 (mercuric sulfate) and H2SO4 to form aldehydes and ketones (According to Markonikov's rule)





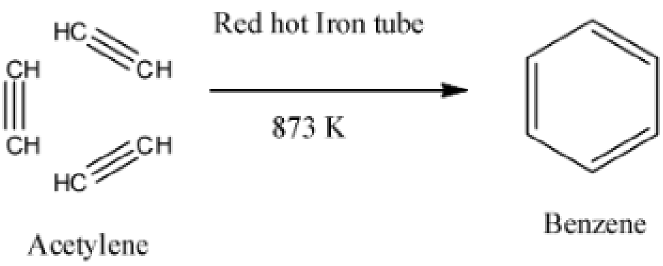
Polymerisation

- **Linear Polymerisation:**



This film of polyethyne (polyaetylene) can be used as electrodes in batteries because it is a good conductor of electricity due to the presence of loosely held electrons.

- **Cyclic Polymerisation:**



Acidic character of alkynes

Terminal alkynes react with strong bases like (sodium metal, sodamide, NaNH2) to form a salt. These reactions explain the acidic nature of alkynes.

$$\underset{\text{Acetylene}}{2HC\equiv CH} + 2Na \longrightarrow \underset{\text{Sodium acetylide}}{2HC\equiv \overset{-}{C}\overset{+}{Na}} + H_2$$

$$\underset{\text{Sodium acetylide}}{2HC\equiv \overset{-}{C}\overset{+}{Na}} + 2Na \longrightarrow \underset{\text{Disodium acetylide}}{2\overset{+}{Na}\overset{-}{C}\equiv \overset{-}{C}\overset{+}{Na}} + H_2$$

Comparison of acidic strength

Ethane		Ethene		Ethyne
CH_3-CH_3	<	$CH_2=CH_2$	<	$CH\equiv CH$
sp3		sp2		sp
sp3		sp2		sp

Acidic strength increase with an increase in electronegativity. Therefore, order of acidic strength - **Ethane < Ethene < Ethyne**

Ethyne > Propyne > Butyne

strong acid

It contains two acidic hydrogen

Aromatisation

Conditions for aromatization: compounds possessing the following characteristics are known as aromatic compounds:

- **Planarity**
- **Complete delocalization of pi-electrons in the ring**

Presence of (4n+2)pi electrons in the ring where (n=1,2,3......). This is referred to as Muckle rule.

Cyclic compounds

Aromatic Compound

Ring

Planar

$(4n + 2)\pi$ e-

[2,6,10,14....]

Anti-aromatic Compound

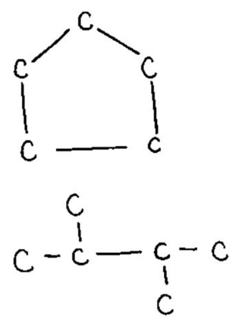
Ring

Planar

$(4n + 2)\pi$ e-

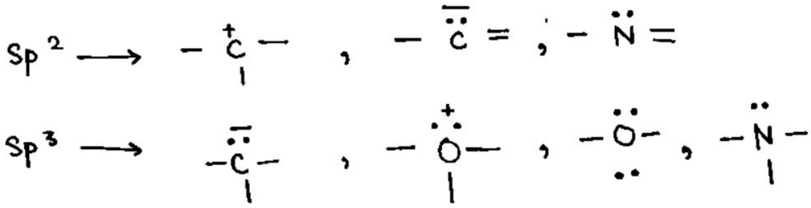
[4,8,12,16.....]

Non-aromatic Compound

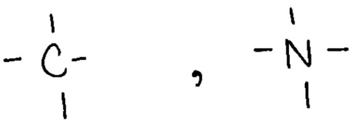


Planar: Atoms which include in ring formation are sp2 hybridised or sp3 hybridised with lone pair.

•For atom (Planar)



Non-Planar:

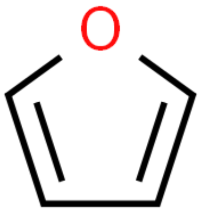


Total pi-electrons: electrons present in the ring to form pi bond.
Lone pair of electrons involve in conjugation in ring.

Q) Identify Aromatic, Antiaromatic and Non-Aromatic compounds

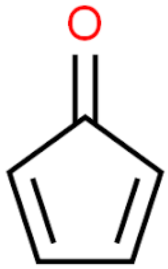
Benzene

Aromatic



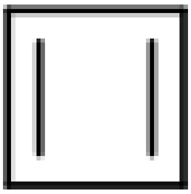
Furan

Aromatic



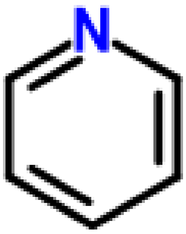
Cyclopenta-1,4-dienone

Anti-aromatic



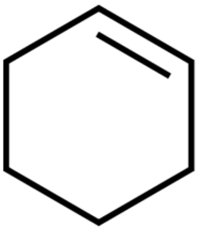
Cyclobuta-1,3 diene

Antiaromatic



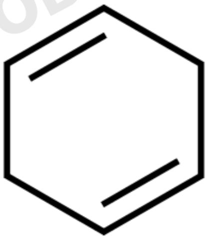
Pyridine

Aromatic



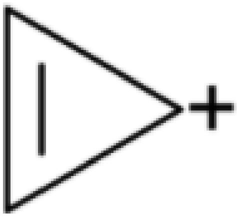
Cyclohexane

Non-Aromatic



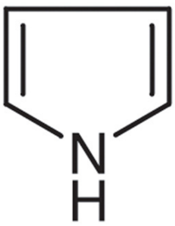
Cyclohexa-1,4-diene

Non-Aromatic



Cyclopropenyl cation

Aromatic



Pyrole

Aromatic

Physical Properties of benzene:

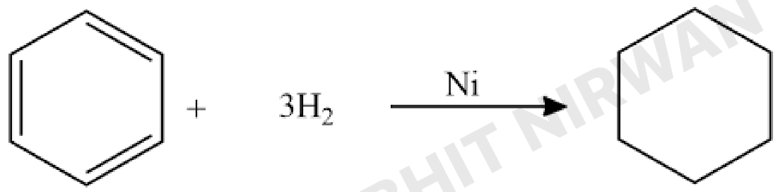
- Benzene is a non-polar molecule and a colorless liquid
- Benzene is insoluble in water because it does not form H-bond with it.

Chemical Properties of benzene:

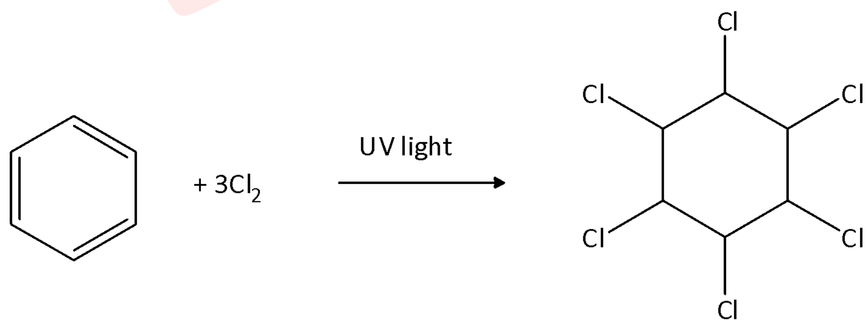
- **Electrophilic addition reaction:** Benzene does not give an electrophilic addition reaction because benzene is stable due to the delocalization of pi-electrons **(i.e pi-electrons are involved in resonance)**

Some addition reactions are as follows:

- At high temperatures and high pressure in the presence of Ni catalyst, hydrogenation of benzene gives cyclohexane.



- Benzene reacts with chlorine in the presence of ultra-violet light to form benzene hexachloride, C6H6Cl6 which is also called gammaxane.

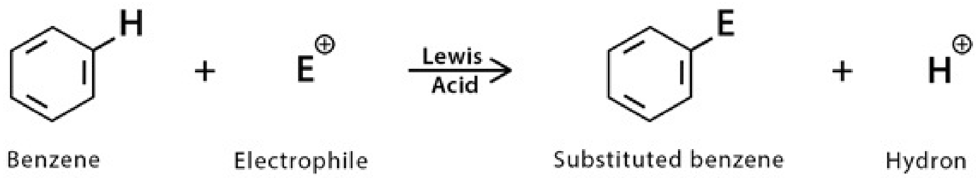


- **Nucleophilic substitution reaction:** Benzene does not give a nucleophilic substitution reaction because benzene is a rich source of pi-electrons and repulsion between pi-electrons and nucleophiles takes place.

- **Combustion:** Benzene burns with a sooty flame in air to produce CO2 and H2O

$$C_6H_6+(15/2)O_2 \rightarrow 6CO_2+3H_2O$$

- **Electrophilic substitution reaction:** Benzene is a rich source of pi-electrons and these pi-electrons involve in resonance. Hence, benzene is extra stable and gives only electrophilic substitution reactions, but not electrophilic addition reactions.

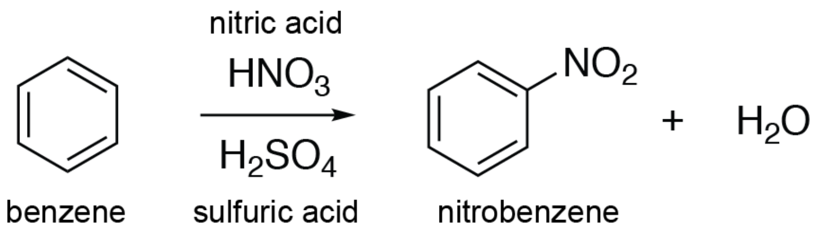


Examples of substitution electrophilic reactions:

- **Nitration:**

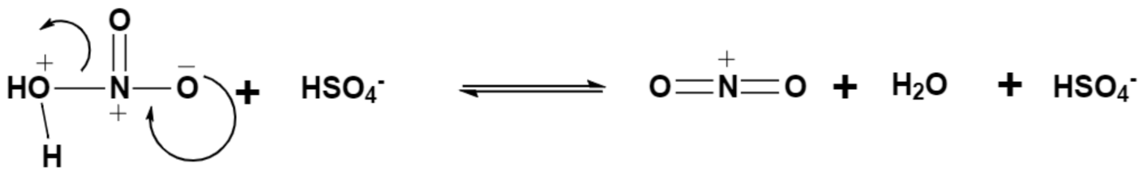
  Reagents- Conc.HNO3 + conc.H2SO4
  Electrophile: NO2+ (nitronium ion)
  Adding species: NO2
  By product: H2O

  When benzene is heated with conc.HNO3 in the presence of conc.H2SO4 gives nitrobenzene, it is known as nitration of benzene.

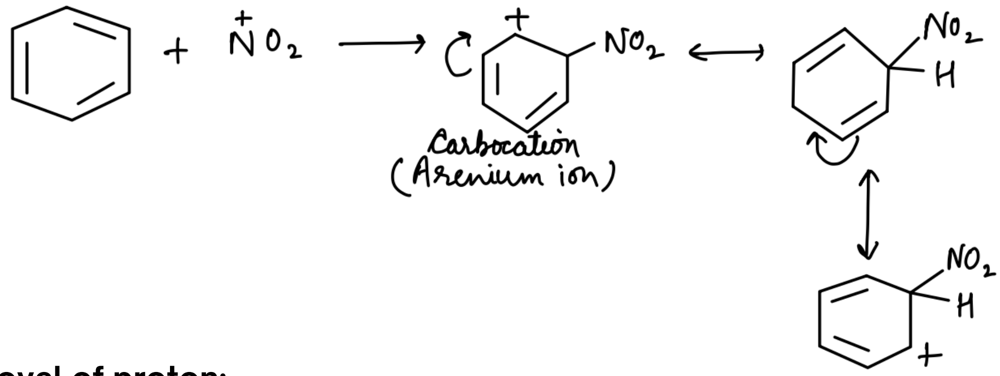


Mechanism of nitration of benzene

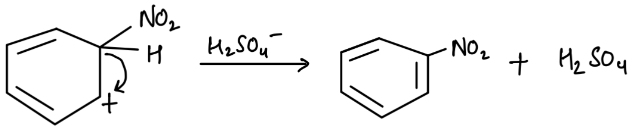
i) Generation of electrophile:

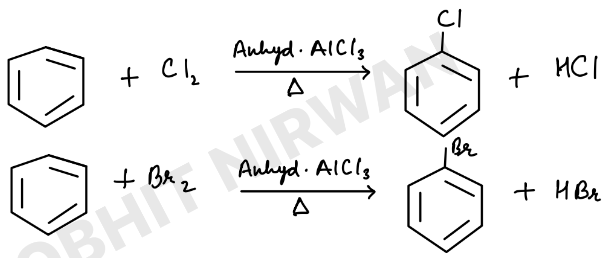


ii) Attack of electrophile on benzene ring to form carbocation:



iii) Removal of proton:





Halogenation

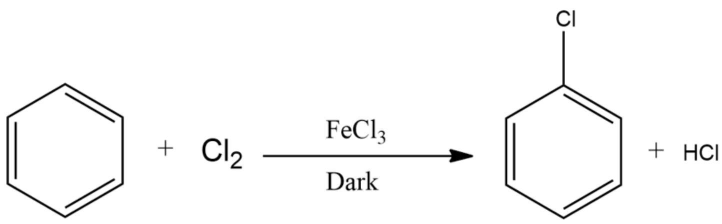
Reagents- Cl2 + Br2 + Anhyd.AlCl3 or Anhyd.FeCl3 or Anhyd. FeBr3

Electrophile: chloronium ion or bromonium ion

Adding species: Cl or Br

By product: HCl or HBr

Benzene reacts with Cl2 or Br2 in the presence of catalyst Anhydr.AlCl3 or FeCl3 or FeBr3 to give chlorobenzene or bromobenzene



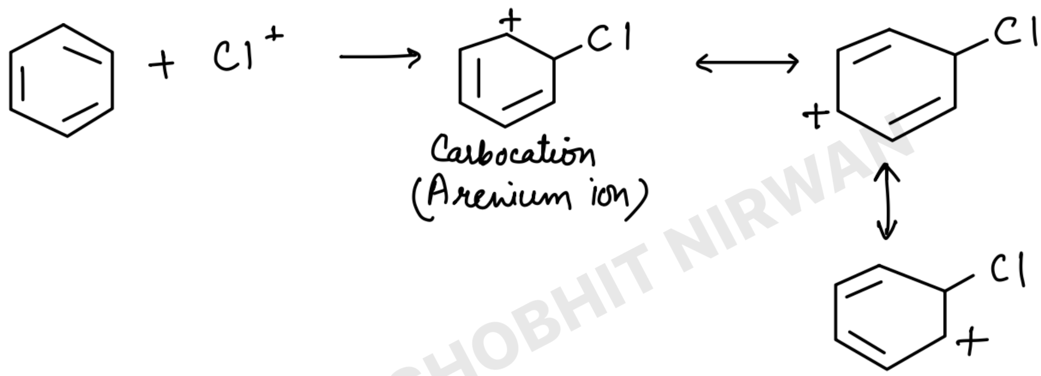
Benzene Chlorobenzene

Mechanism of chlorination of Benzene

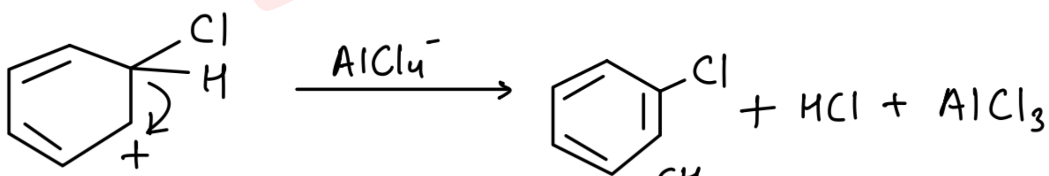
i) Generation of electrophile:

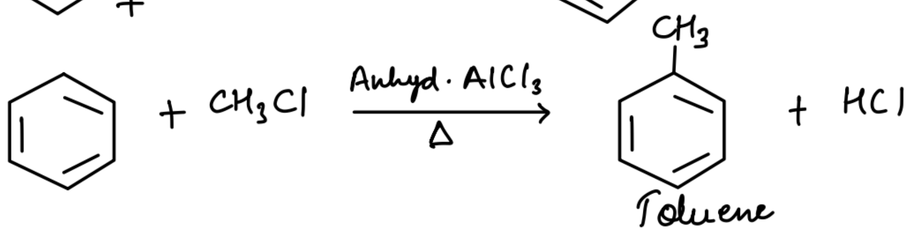
$$Cl - Cl + AlCl_3 \dashrightarrow Cl^+ + AlCl_4^-$$

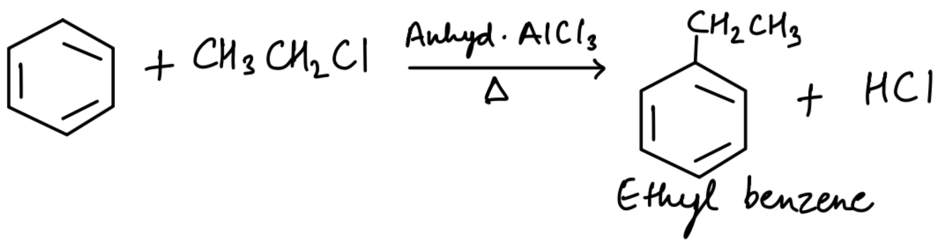
ii) Attack of electrophile on benzene ring to form carbocation



iii) Removal of proton:



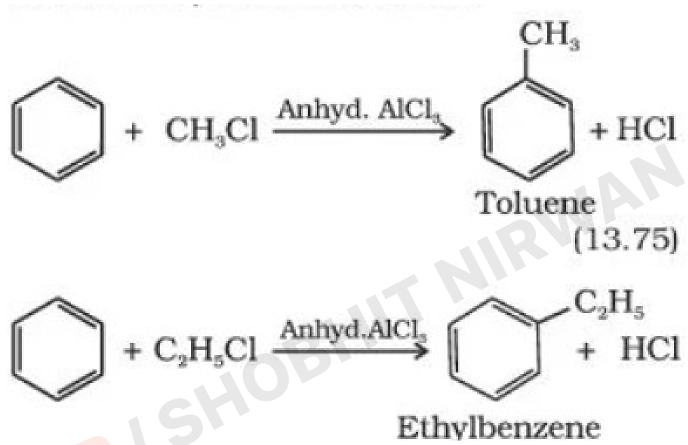




Fridel Craft Alkylation

Reagent- RCl + Anhyd AlCl3 (where R = CH3, C2H5, C3H9 etc.)
Electrophile- R+ (carbocation)
Adding reaction- R
Byproduct- HCl

When benzene reacts with chloroalkane in the presence of catalyst like anhyd. AlCl3 to form alkyl benzene.

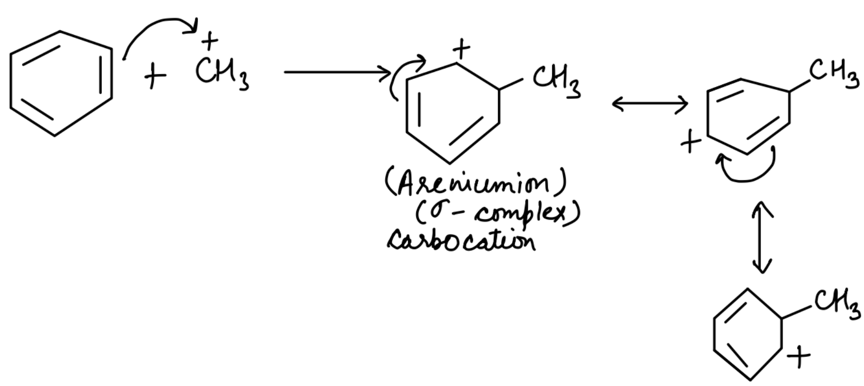


Mechanism of Fridel Craft Alkylation

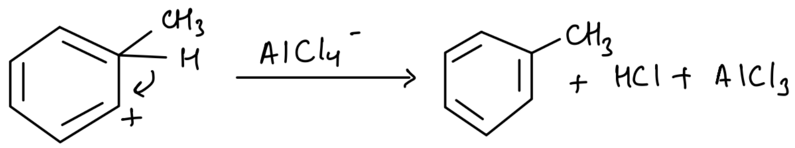
i) Generation of electrophile:

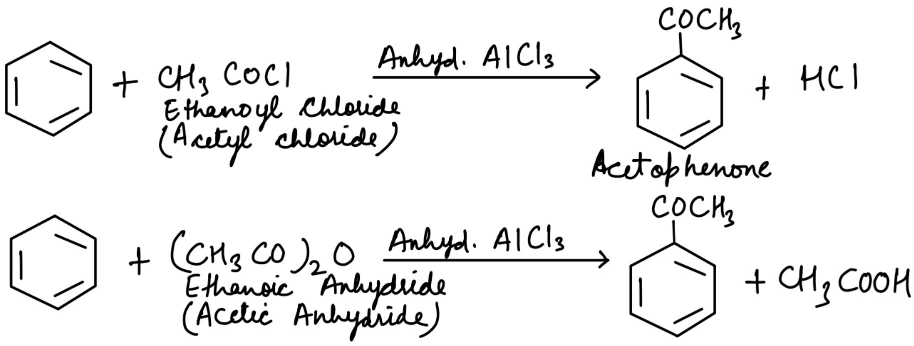
$$CH_3 - CL + AlCl_3 \text{-------}> CH_3^+ + AlCl_4^-$$

ii) Attack of electrophile on benzene ring to form carbocation



iii) Removal of proton:





Fridel Craft Acylation

CH3CO - Acetyl or acyl

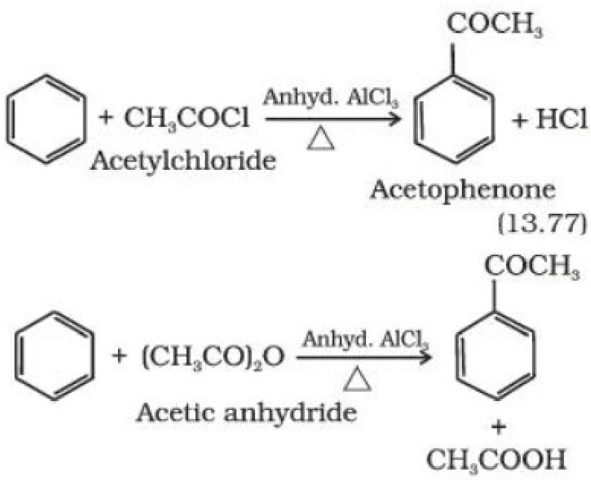
Reagent- CH3COCl + Anhyd.AlCl3 or (CH3CO)2 + Anhyd.AlCl3

Electrophile- COCH3 (Acylium ion)

Adding species- COCH3

Byproduct- HCl or CH3COOH

When benzene reacts with acetyl chloride (CH3COCl) or acetic anhydride, (CH3CO)2 in the presence of catalyst like anhyd.AlCl3, to form acetophenone

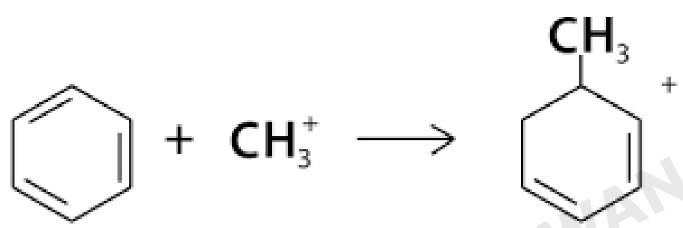


Mechanism of Fridel Craft Acylation

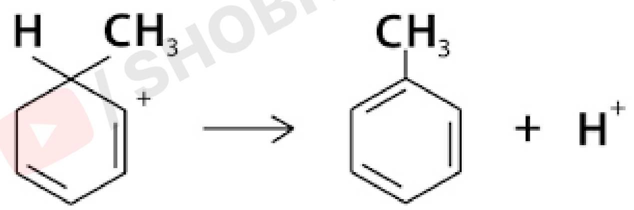
i) Generation of electrophile

$$CH_3-Cl + Al-Cl_3 \rightleftharpoons CH_3^+ + AlCl_4^-$$

ii) Attack of electrophile on benzene ring to form carbocation



iii) Removal of proton:

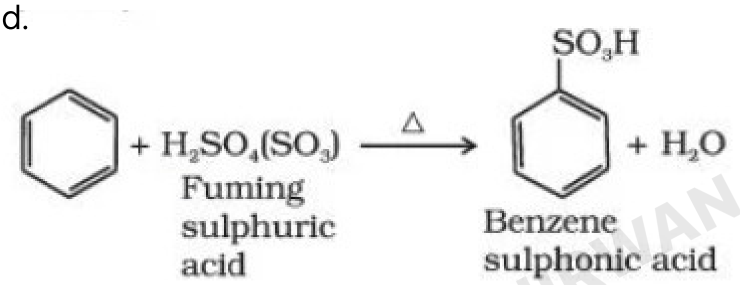


$$H^+ + AlCl_4^- \longrightarrow HCl + AlCl_3$$

Sulphonation

Reagents- Conc.H2SO4 or Fuming H2SO4 or SO3 + H2SO4 OR H2S2O7 (Oleum)
Electrophile: SO3
Adding species: SO3H
By product: H2O

When benzene is reacted with conc.H2SO4 or oleum to form benzene sulphonic acid.

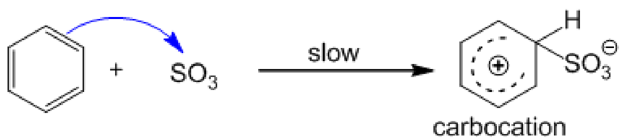


Mechanism of sulphonation or Benzene

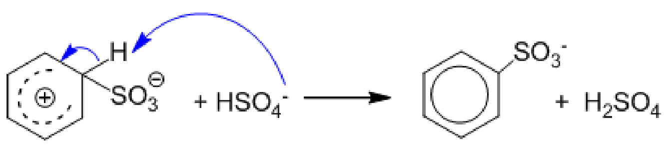
i) Generation of electrophile

$$2\ H_2SO_4 \overset{slow}{\rightleftharpoons} SO_3 + H_3O^+ + HSO_4^-$$

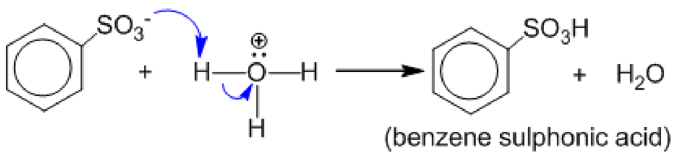
ii) Attack of electrophile on benzene ring to form carbocation



iii) Removal of proton:

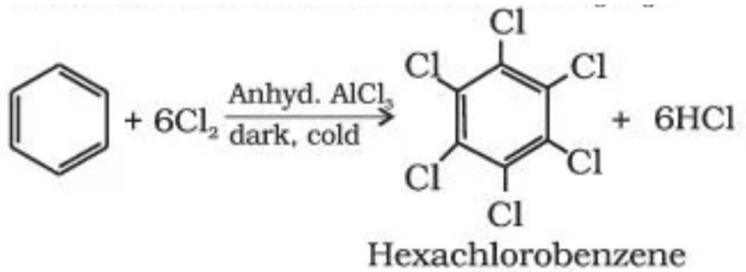


iv) Protonation



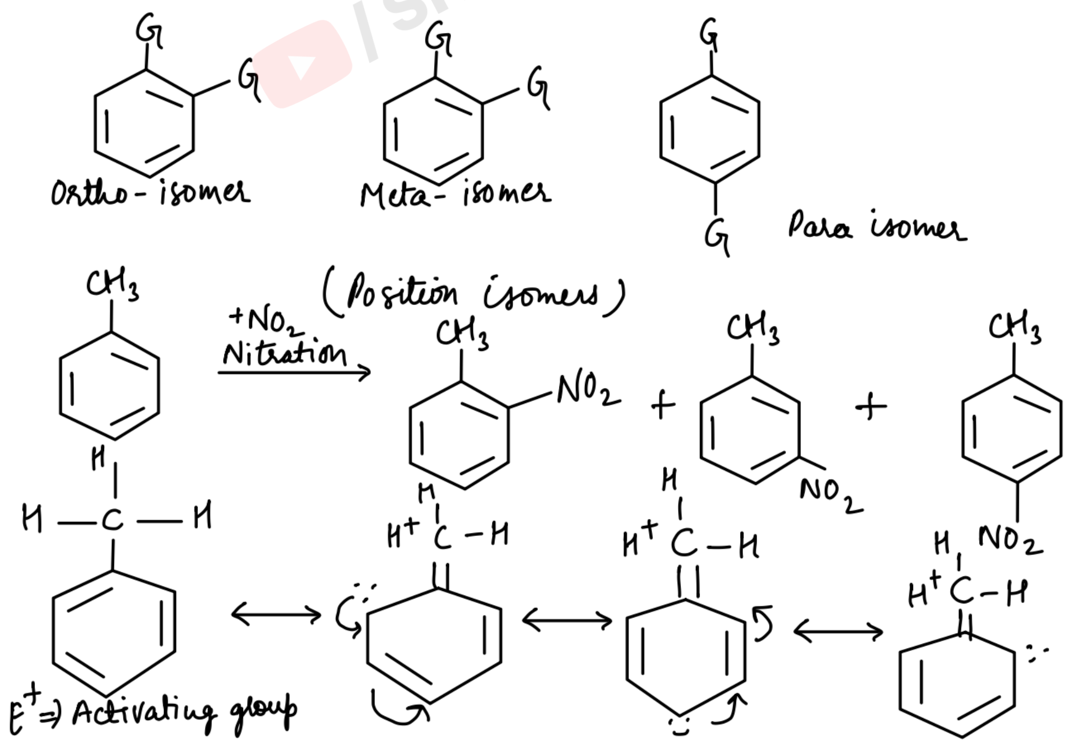
Importance:

- If excess of electrophilic reagent is used, further substitution reaction must take place

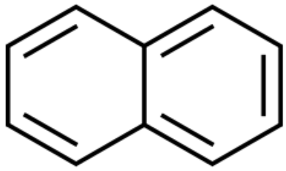


Hexachlorobenzene
(C_6Cl_6)
(13.79)

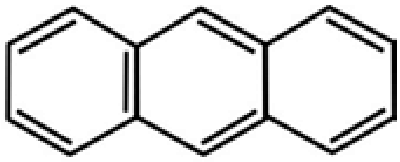
S.E reactions in mono-substituted benzene



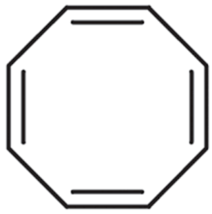
Napthalene



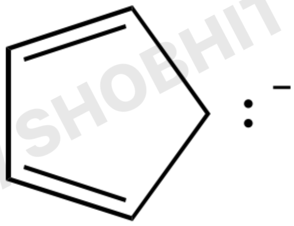
Anthracene



Cyclooctatetraene

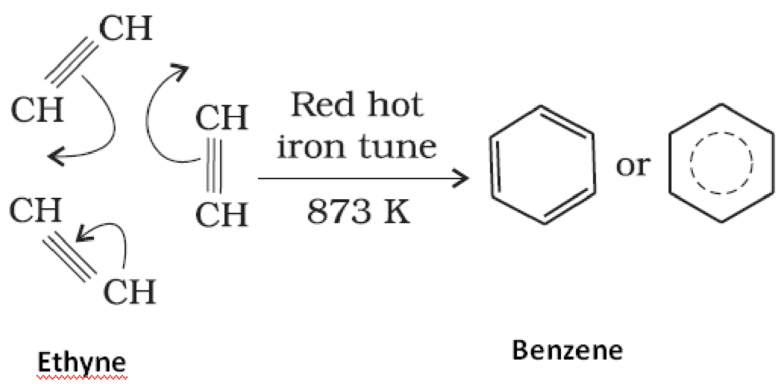


Cyclopentadienylanion

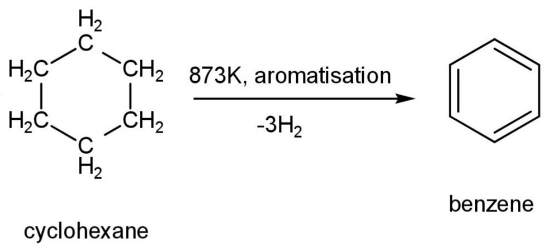


Preparation of benzene

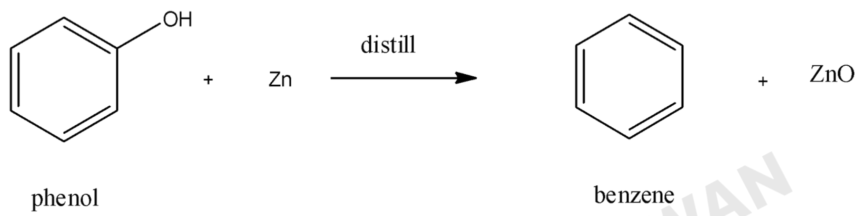
a.) From Ethyne:



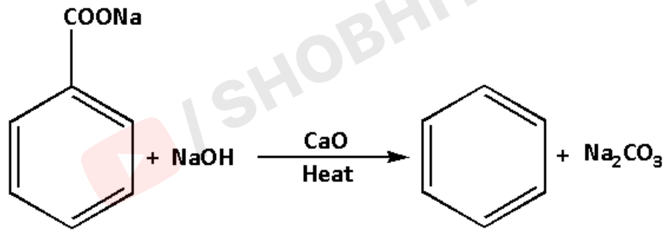
b.) Aromatisation



c.) From phenol

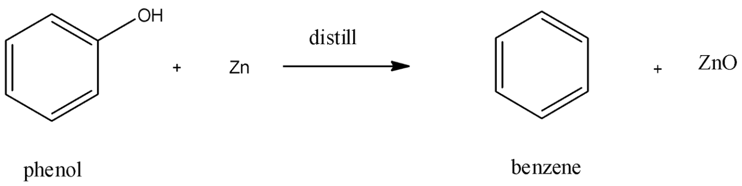


d.) From sodium benzoate

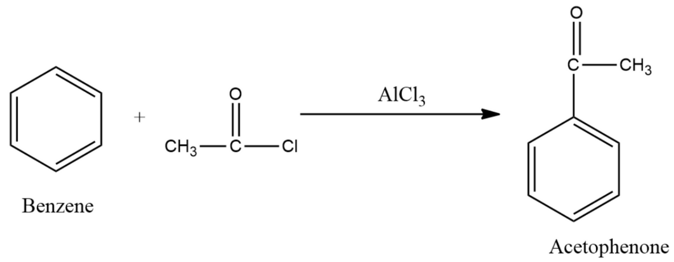


Q. Complete the following reactions:

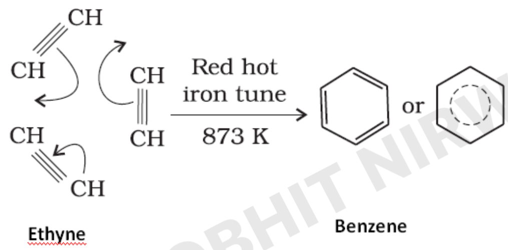
a.)



b.)

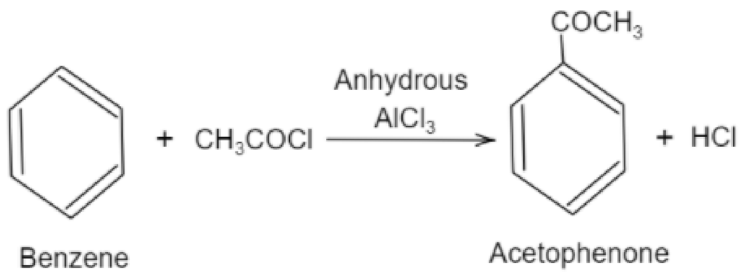


c.)

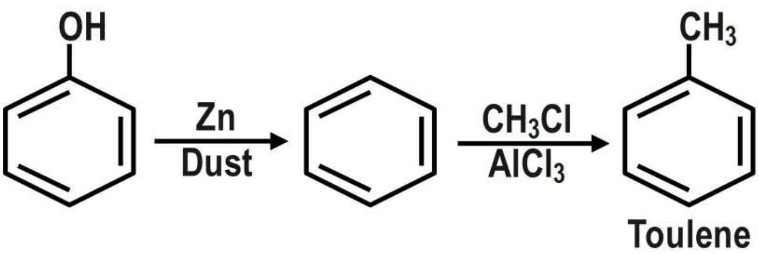


Q.Convert:

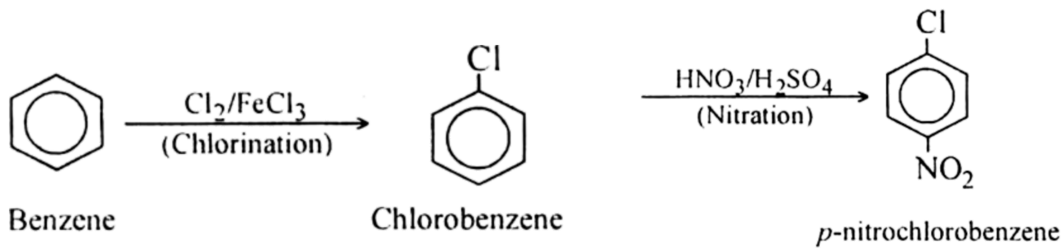
a.) Benzene to acetophone



b.) Phenol to Toluene



c) Benzene into nitrochlorobenzene



d.) Benzene to m-nitrotoluene